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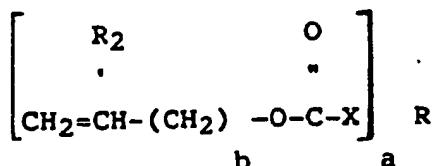
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(54) Novel vinyl carbonate and vinyl carbamate contact lens material monomers.

(57) Novel monomers of the general formula



where b is 0 or 1, a is 1, 2, 3 or 4, R² is a monovalent alkyl radical and R is an organic radical. The novel monomers may be employed to produce novel copolymers useful as hydrogel, soft non-hydrogel and/or rigid gas permeable contact lens materials.

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NOVEL VINYL CARBONATE AND VINYL CARBAMATE CONTACT LENS MATERIAL MONOMERS

BACKGROUND OF THE INVENTION

Biomedical materials which are particularly useful as contact lens materials fall into three general
 5 classifications; hydrogels, non-hydrophilic soft materials and rigid gas permeable materials.

The chemistries of contact lens hydrogels are almost completely described by polymer and copolymer systems comprised of either 2-hydroxyethylmethacrylate (HEMA) or N-vinyl-2-pyrrolidinone (NVP), or mixtures of HEMA and NVP. Minor components such as crosslinking agents are used in these systems to control tear strength, hydrolytic stability, modulus, etc. These hydrogel systems are generally well known
 10 and have been successful on a commercial basis, but they are not without shortcomings.

Polysiloxane based elastomers have also been known in the contact lens art for some time and have enjoyed limited commercial success. In general, the silicone chemistries involve vinyl functional end capped polysiloxane polymers.

Rigid gas permeable contact lens materials are generally copolymers formed from copolymerizing
 15 acrylic or methacryl functional monomers which contain siloxane functionalities and often also contain fluorine atoms.

The present invention provides a novel monomer chemistry to the art of biomedical device materials.

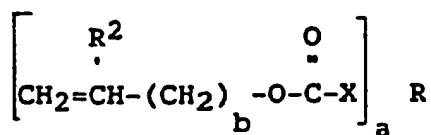
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SUMMARY OF THE INVENTION

The present invention provides novel monomers useful in biomedical devices. These novel monomers have the general formula

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where b is 0 or 1, a is 1, 2, 3 or 4, R² is a monovalent alkyl radical and R is an organic radical. The novel monomers may be employed to produce novel copolymers useful as hydrogel, soft non-hydrogel and/or
 35 rigid gas permeable contact lens materials.

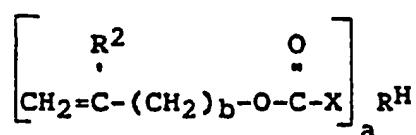
DETAILED DESCRIPTION OF THE INVENTION

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The present invention is directed to new crosslinked copolymers which employ novel monomers also disclosed in this application. These novel copolymers are particularly useful as biomedical materials, and are especially useful in the area of contact lens applications. These new crosslinked copolymers, when used in contact lens applications, can produce a wide variety of types of contact lens materials ranging from hard, gas permeable lens materials; soft, hydrogel lens materials; to soft, non-hydrogel lens materials.
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The novel monomers generally fall into the following classifications: a) hydrophilic monomers with the general formula

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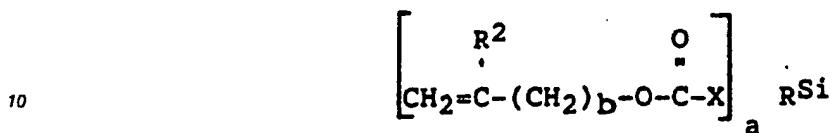


where b is 0 or 1; a is 1, 2, 3 or 4

X denotes -NH-, -S- or -O-; and

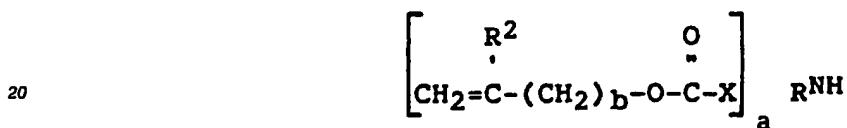
R^H denotes a hydrophilic moiety such as an organic radical with one or more amide hydroxyl, urea or carboxylic acid functionalities so that the monomer as a whole is relatively hydrophilic;

- 5 b) silicone containing monomers of the general formula



where a, b, and X are defined as above and R^{Si} denotes a silicone containing organic radical;

- 15 c) non- or slightly hydrophilic monomers of the general formula



where a, b and X are as defined above and R^{NH} denote a non-hydrophilic organic radical.

25 In general, there are no clear-cut demarcations between any of the three classifications of contact lens materials. However, in general, hydrogel materials should have oxygen permeabilities with DK's greater than $20 \times 10^{-11} \text{ cm}^3 \times \text{cm/sec.} \times \text{cm}^2 \times \text{mmHg}$ (or DK units hereinafter) and preferably greater than 40 DK and most preferably greater than 60 DK. They should have a Young's modulus of elasticity in the range of 20 to 400 g/mm², preferably 50 to 200 g/mm² as measured by ASTM test method D 638. They should have tear strengths greater than 1 g/mm² and preferably greater than 5 g/mm² as measured by ASTM test method D 1938. Their water content should be between 10 to 80%, and preferably between 20 to 50%. The contact angle, which is a measurement of the wettability of the lens, should be less than 80° and should preferably be less than 40°. The protein uptake of hydrogel lenses or hydrogel lens materials should be less than or equivalent to that of PHEMA.

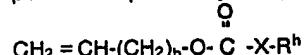
35 Soft, non-hydrogel materials should have at a minimum oxygen permeabilities equal to or greater than hydrogel materials. The water content should always be less than 10%, and preferably less than 5%. The modulus of elasticity should be between 20 and 5,000 g/mm² and preferably should be in the range of 50 to 250 g/mm². Contact angle should be less than 80 and preferably less than 40° and the tear strength (both initial and propagation) of this material should be in excess of 5 g/mm².

40 Properties of hard, gas permeable lens materials should be similar to that of the hydrogel and the soft, non-hydrogel materials. In addition, the glass transition temperature of such materials should be greater than 40°C and preferably greater than 65°C. The modulus of the material should be greater than 50,000 g/mm² and preferably greater than 75,000 g/mm².

45

HYDROGEL MATERIALS

To prepare a soft, non-hydrogel material the following prepolymer formulations should be used: (a) between 25 and 90% of the prepolymer mixture should comprise a hydrophilic monomer portion. This portion will preferably comprise in part at least a hydrophilic monomer represented by the general formula



where b is 0 or 1 and X is -S-, -O-, or -NR³⁻ and R^h denotes a relatively hydrophilic moiety. This hydrophilic

55 monomer portion may also include at least one of the hydrophilic monomers chosen from the group consisting of wetting monomers N-vinyl-2-pyrrolidinone, 2-hydroxyethyl vinyl carbonate, 2-hydroxyethyl vinyl carbamate, 3-(2-pyrrolidinone-1-yl)propyl vinyl carbonate, 2-(2-pyrrolidinone-1-yl)ethyl vinyl carbonate, N-(vinyloxycarbonyloxy)pyrrolidin-2,5-dione, N-[vinyloxycarbonyloxyethyl]pyrrolidin-2,5-dione,

vinyacetamide, N-methyl-N-vinyacetamide, N,N-dimethyl vinyl carbamate, N,N-diethyl vinyl carbamate. These monomers may, of course, comprise only a portion of the hydrophilic monomer portion of prepolymer mix which can further be comprised of other hydrophilic monomers.

The hydrogel prepolymer formulation should also preferably contain a non- or weakly hydrophilic monomer as combination of monomers chosen from the group consisting of 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, t-butyl vinyl carbonate, t-butyldimethylsiloxyethyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate, 3-(vinyloxycarbonylthio)propyl[tris(trimethylsiloxy)silyl]silane, 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate, t-butylphenyl vinyl carbamate. These non- or slightly hydrophilic monomers enhance the oxygen permeability of the final copolymer.

10 The hydrogel prepolymer compositions further comprise (c) between about 0.1 to 10% of a crosslinking agent, which may be chosen from a list of preferred crosslinking agents later disclosed in this application, or one of the crosslinking monomers known in the prior art as exemplified and/or taught in U.S. Pat. Nos. 4,060,678; 4,182,822; 4,267,295; 4,640,941 and/or 4,690,993.

15 The amount of hydrophilic monomer used to prepare the hydrogel material in the present invention is adjusted within the above limits to give a water content in the hydrated hydrogel of from about 5 to approximately 80% by weight. The non- or weakly hydrophilic monomer content is adjusted to maximize other desirable properties such as oxygen permeability, modulus and/or tear strength. The quantity of the crosslinking monomer used to produce a hydrogel material is adjusted to maximize desirable properties such as water content, modulus, lens strength, and also aids in the hydrolytically stability of the final 20 material. In addition, UV absorbing monomers or tinting monomers may also be added to enhance the properties of the final material.

For instance, the following prepolymer formulations would produce hydrogel materials within the scope of the present invention.

- I. A. 25-90 wt% hydrophilic monomer, 2-hydroxyethyl vinyl carbamate;
- 25 B. 10-30 wt% non- or weakly hydrophilic monomer 3-N-[tris(trimethylsiloxy)silylpropyl] vinyl carbamate; and
- C. 0.1-10 wt% crosslinker, 1,2-bis(vinyloxy carbonyloxy)ethane.
- II. A.i) 25-90 wt% hydrophilic monomer 2-hydroxyethyl vinyl carbamate; and
- ii) 25-90 wt% hydrophilic monomer N-vinyl pyrrolidinone, where the combination of i and ii comprises 30 between 25 to 90 wt% of the final prepolymer compositions.
- B. 10-90 wt% of non-, or weakly hydrophilic monomer t-butyldimethylsiloxyethyl vinyl carbamate; and
- C. 0.1-10 wt% crosslinker, α,ω -bis(vinyloxycarbonyl) polyethylene glycol.
- III. A. 25-90 wt% hydrophilic monomer, 3-(2-pyrrolidinon-1-yl)propyl vinyl carbamate;
- B. 10-30 wt% weak or non-hydrophilic monomer, t-butyl vinyl carbamate; and
- 35 C. 0.1-10 wt% crosslinker, α,ω -bis(vinyloxycarbonyl) polyethylene glycol.

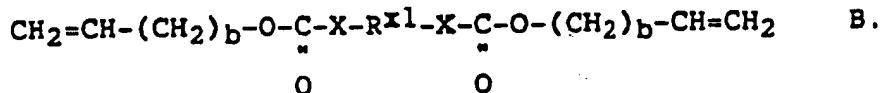
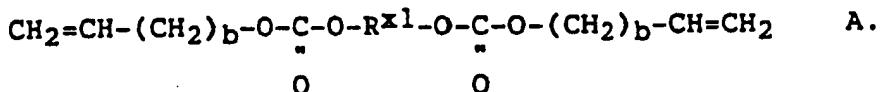
HARD, GAS PERMEABLE MATERIALS

40 Hard lenses are prepared using: (I) one or more of the non-hydrophilic monomers of the present invention; (II) a crosslinking agent; (III) a small amount of a wetting monomer; and (IV) optionally other agents such as strengthening agents or UV absorbing or dye monomers. The three main components are used in the following ratios: the non-hydrophilic monomer component (I) is used in amounts of about 60 to about 95 weight percent, the crosslinking monomer (II) in amounts from 0.1 to 10 weight percent, and the wetting monomer (III) in amounts from about 1 to 20 weight percent. The content of the crosslinking agent is chosen to provide a dimensionally stable lens material resistant to breakage and stress crazing. The amount of wetting monomer used is adjusted within limits to provide sufficient wetting characteristics so as to maintain a stable tear film while at the same time keeping a sufficiently low water content.

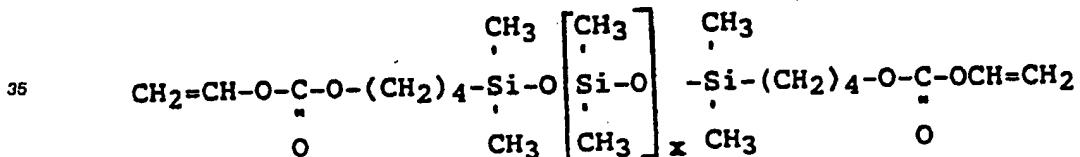
50 The non-hydrophilic monomers used to make the hard contact lens materials include one or more of the following monomers: 2,2,2-trifluoroethyl vinyl carbonate, 2,2,2-trifluoroethyl vinyl carbamate, 1,1,1,3,3,3-Hexafluoroprop-2-yl vinyl carbonate, 2,2,2-trifluoroethyl allyl carbamate, 2,2,2-trifluoro-1-phenylethyl vinyl carbonate, trimethylsilylmethyl vinyl carbonate, trimethylsilylethyl vinyl carbonate, 3-(trimethylsilyl)propyl vinyl carbonate, t-butyldimethylsiloxyethyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, 3-[tris-(trimethylsiloxy)silyl] propyl vinyl carbamate, 3-(vinyloxycarbonylthio) propyl-[tris(trimethylsiloxy)silyl]silane].

The crosslinking agents used preferably to make hard contact lens materials include crosslinking agents known in the prior art as taught in the U.S. patents referenced supra, but most preferably crosslinking

agents chosen from the group consisting of crosslinking monomers represented by the formula



- 20 wherein: X denotes -S-, -O-, or -NH- and at least one X denotes a -NH- in formula B; b is 0 or 1;
 R^{c1} denotes a multivalent organic radical and a is 2, 3, or 4; and R^{x1} denotes a divalent organic radical.
- The preferred crosslinkers includes:
- 1,5-bis(vinyloxycarboxyloxy)-2,2,3,3,4,4-hexafluoropentane;
 - 1,2-bis(vinyloxycarboxyloxy)ethane;
 - α,ω -bis(vinyloxycarbonyl)polyethylene glycol;
 - 25 N,O-bis(vinyloxycarbonyl)ethanolamine;
 - 2,2' dimethyl-1,3-bis(vinyloxycarbonyloxy)propane;
 - α,ω -bis-(vinyloxycarbonyl)triethylene glycol;
 - 2,2-dimethyl-N,N-bis(vinyloxycarbonyl)-1,3-propandiamine;
 - 1,3-bis-[4-(vinyloxycarbonyloxy)but-1-yl] tetramethylidisiloxane;
 - 30 N,N-bis-(vinyloxycarbonyl)-1,6-diaminohexane;



- 40 where X = 25 on the average.
The wetting monomers useful in hard contact lenses include N-vinylpyrrolidinone, 2-hydroxyethyl-methacrylate, itaconic acid, methacrylic acid, N,N-diethylacrylamide, N,N-diethyl vinyl carbamate, N,N-dimethyl vinyl carbamate, N-Methyl-N-Vinyl acetamide, and all hydrophilic monomers listed in the hydrogel section supra.
- 45

SOFT, NON-HYDROGEL MATERIALS

- 50 Soft, non-hydrogel contact lens materials with little or no water content can be prepared by polymerizing prepolymer mixtures with the following formulations: between 50 and 90 weight percent of non-hydrophilic monomers with the following general formula:



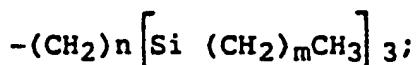
where X d notes either -O-, -S- or -NH-; and

R^{NH} represents an organic radical that is largely non-hydrophilic, and a is 1, 2, 3 or 4; from 5 to about 25 weight percent of a hydrophilic monomer and between 0.1 and about 10% of a crosslinking monomer.

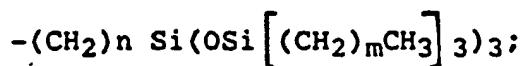
5 R^H, the largely non-hydrophilic moiety in the above formula, is typically a monovalent radical - but it may be multivalent. The main functional requirement is that it is largely non-hydrophilic, generally nonreactive to free-radical vinyl addition reactions and may be incorporated into the above formula from a synthetic perspective.

In general, R^{NH} may be described by the following formulae:

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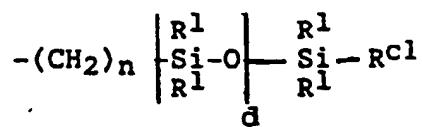
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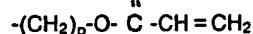


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where R¹ denotes a monovalent organic radical such as an alkyl radical with 1 to 6 carbon atoms, or a fluoroalkyl radical with 1 to 6 carbon atoms;

30 R^{Cl} denotes



p is 1 to 6; and

d is 1-200, and

35 where n is 1, 2, 3 or 4, m is 0, 1, 2, 3, 4, or 5, or R^{NH} denotes a partially or fully fluorinated alkyl, alkylaryl or aryl radical.

The non-hydrophilic monomers specifically include 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; 1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyldisiloxane; 3-(trimethylsilyl)propyl vinyl carbonate; t-butyl-dimethylsiloxyethyl vinyl carbonate; trimethylsilylmethyl vinyl carbonate; trimethylsilylethyl vinyl carbonate; 2,2,2-trifluoroethyl vinyl carbonate; t-butyl vinyl carbonate; 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbonate; 2,2,2-trifluoroethyl vinyl carbamate; 1,1,1,3,3-hexafluoro-2-propyl vinyl carbonate; 3-(vinyloxycarbonylthio)-propyl-[tris(trimethylsiloxy)silane]; 3-[tris-(trimethylsiloxy)silyl]propyl vinyl carbamate; "V₂D₂₅", 2,2,2-trifluoro-1-phenylethyl vinyl carbonate; 1-adamantane vinyl carbonate, 1-adamantanemethyl vinyl carbonate, 1-adamantaneethyl vinyl carbonate; and 1-adamantane vinyl carbamate.

45 The hydrophilic monomers used to produce the proper wetting conditions in combination with the soft non-hydrogel materials are selected from hydrophilic monomers used in contact lenses in general, including N-vinyl lactams eg, N-vinyl pyrrolidinone; hydroxyalkyl acrylates and methacrylates such as 2-hydroxyethyl methacrylate (HEMA) and preferably, the hydrophilic vinyl carbonates and vinyl carbamates disclosed in this application such as hydroxyethyl vinyl carbonate; N,N-dimethyl vinyl carbamate; or N-hydroxyethyl vinyl carbamate; N-[vinyloxycarbonyloxyethyl] pyrrolidin-2,5-dione; and 3-(2-pyrrolidinon-1-yl)propyl vinyl carbonate.

50 Crosslinkers used for the soft, non-hydrogel contact lens materials include the crosslinkers known in the prior art such as m thylene glycol dimethacrylate and divinylbenzen, but preferably are crosslinking agents described in the present application by formulas A, B and C.

55 The preferred non-hydrophilic monomers are the long chain siloxane monomers of the present invention such as the so-called "V₂D₂₅" monomers.

Some examples of soft non-hydrogel prepolymer formulations include:

- 1) 80 wt% V₂D₂₅;
 10 wt% N-vinyl-2-pyrrolidinone;
 5 wt% 2,2,2-trifluoroethyl vinyl carbonate; and
 5 wt% N-O-bis-(vinylcarbonyl)ethandamine.
- 5 II) 60 wt% 3-(trimethylsiloxy)propyl vinyl carbonate;
 30 wt% α,ω -bis(vinyloxycarbonyl) polyethylene glycol;
 5 wt% 1,1,1,3,3-Hexafluoroprop-2-yl vinyl carbonate; and
 5 wt% N-vinyl-N-methyl acetamide.
- III) 25 wt % 3-(trimethylsilyl)propyl vinyl carbonate;
- 10 64 wt % 3-[tris-(trimethylsiloxy)silyl]propyl vinyl carbamate;
 10 wt% N-vinylpyrrolidinone; and
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy) propane.
- IV) 20 wt% t-butylidimethylsiloxyethyl vinyl carbonate;
 70 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate;
- 15 9 wt% N-vinylpyrrolidinone; and
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy) propane.
- V) 20 wt% trimethylsilyl vinyl carbonate;
 69 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate;
 10 wt% N-vinylpyrrolidinone; and
 20 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy) propane.

The copolymers of the present invention are formed by way of a free radical polymerization the details of which are generally known in the art. In general, the various comonomers are chosen and combined, as required to form the desired final copolymers, and a free radical catalyst is added to the mixture. The mixture is then polymerized to form the desired copolymer.

- 25 Free radical catalysts are known in the art and are mostly of two general types: heat initiated free radical catalysts, and photoinitiated free radical catalysts, more specifically, ultraviolet radiation initiated free radical catalysts. Heat initiated catalysts include peroxides such as 2,5-dimethyl-2,5-bis(2-ethylhexanoyl-peroxy) hexane (Lupersol 256TM Pennwalt Chemicals), bis(isopropylperoxy) dicarboxate, acetylperoxide, lauroyl peroxide or benzoyl peroxide, photoinitiators include compounds such as 2-hydroxy-2-methyl-1-phenylpropan-1-one (DarocurTM, EM Chemicals), and the like.

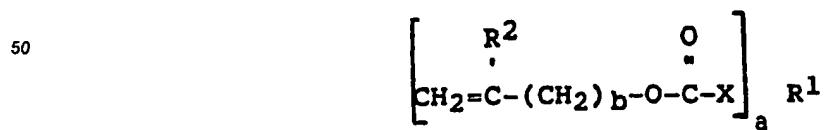
30 Diluents may be employed in the process of polymerizing the copolymers of the present invention in order to modify the resultant physical characteristics of the finished copolymer. For instance, the comonomer mixture used to produce a hydrogel like material may also include a portion of methylethylketone. In general, the amount of diluent used should be less than 50 wt%. In most cases, the diluent content will be less than 30 wt%. In a particular copolymer system, the actual limit will be dictated by the solubility of the various comonomers in the diluent. In order to produce an optically clear copolymer, it is important that a phase separation does not occur between the comonomers and the diluent, or the diluent and the final copolymer.

35 Furthermore, as a practical matter, the maximum amount of diluent which may be used will depend on the amount of swelling the diluent causes the final copolymers. Excessive swelling will or may cause the copolymer to collapse when the diluent is replaced with water upon hydration.

40 Suitable diluents include ethyleneglycol; glycerine; liquid polyethyleneglycol; alcohols; alcohol/water mixtures; ethylene oxide/propylene oxide block copolymers; low molecular weight linear polyhydroxyethyl-methacrylates; glycol esters of lactic acid; formamides; ketones; dialkylsulfoxides; butyl carbitol; and the like.

45 These novel copolymers in general are made from polymerizing mixtures comprising:

a) from 1 to 99 wt.% of a base monomer of the general chemical formula



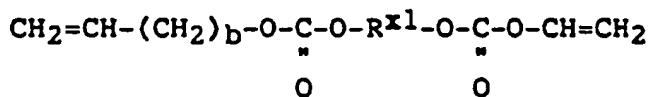
55 wherein: X denotes an -O-, -S-, or -NR³- divalent radical;
 R¹ denotes an organic radical;
 R² denotes -H or -CH₃;

R³ denotes -H, or a monovalent alkyl radical;

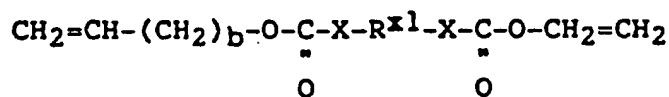
a is 1, 2, 3, or 4; and

b is 0 or 1.

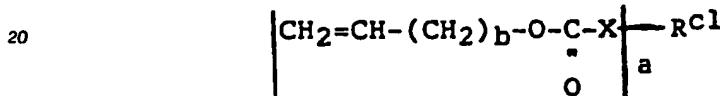
- 5 b) from 0.1 to 20 wt.% of a crosslinking agent known in the biomedical material art, or a novel crosslinker represented by the chemical formulae:



or



or



25 wherein: X is -O- or -NH- with at least one X being -NH-; R^{c1} denotes a multivalent organic radical, b is 0 or 1, and a is 2, 3 or 4.

These copolymers may also contain further additives such as wetting agents, tints, dyes, strengthening agents and the like to tailor specific material properties as desired.

30 The copolymers of the present invention are useful as biomedical devices, and in particular, are well suited as contact lens materials. The copolymers can be formed into contact lenses by many of the techniques known in the art to be useful in contact lens production. For instance, prepolymer mixtures containing heat initiated free radical catalysts can be placed in polypropylene tubes which are then heat cured over time to form copolymeric rods which are then cut to form button shaped articles. These button shaped articles can then be lathed into contact lenses.

35 Alternately, the prepolymer mixture can be molded per the methods disclosed in U.S. Patent Nos. 4,085,459 or 4,197,266. Spin casting techniques may also be used with the present materials and such methods as described in U.S. Patent Nos. 3,408,429 and 3,496,254 can be so adopted to be useful with the present copolymers.

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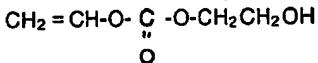
SYNTHESIS OF MONOMERS

PART I - SYNTHESIS OF HYDROXALKYL MONOMERS USEFUL AS HYDROGEL BASE MONOMERS AND WETTING AGENTS

50 1.0 2-Hydroxyethyl Vinyl Carbonate C₆H₈O₄

To a 1000mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N₂ blanket, thermometer, and a dropping funnel 5.0g (81.66mmol) of ethylene glycol, 7.12g (90.0mmol) of pyridine and 500mL of chloroform were added. To this reaction mixture 8.77g (81.66mmol) of vinyl chloroformate was added over 20 minutes. The reaction mixture was stirred for 16 hours. The volume of the mixture was reduced to 75mL on a rotary evaporator and the residue washed with 100mL of 2N HCl. The aqueous phase was set aside. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was purified by chromatography (silica gel, gradient starting with 60%

cyclohexane 40% chloroform) to give an oil. The 2N HCl wash was saturated with sodium chloride and extracted three times with 50mL chloroform. The combined chloroform extracts were dried with magnesium sulfate and flash evaporated to an oil. The oils combined to give 2.3g (17.4mmol, 21.3%) of a light yellow oil. FTIR (neat, capillary) 3500.56, 3477.38, 3379.94, 2960.20, 1805.29, 1753.69, 1650.79, 1558.65, 1540.44, 5 1506.71, 1481.33, 1455.89, 1388.72, 1373.25, 1299.19, 1244.25, 1154.19, 1067.30, 1015.59, 995.52, 969.77, 944.14, 913.44, 875.08, 859.65, 779.15, 717.53, 684.06, 666.45, 649.43. NMR (CDCl_3) δ 6.83-7.177 (1H,m), 4.56-5.0 (2H,m), 4.13-4.37 (2H,m), 3.70-3.93 (2H,m), 3.07-3.43 (1H,s). The instrumental analyses were consistent with a compound represented by the following formula:

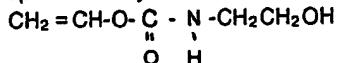


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1.1 2-Hydroxyethyl Vinyl Carbamate $\text{C}_5\text{H}_9\text{NO}_3$

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To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N_2 blanket, thermometer, and dropping funnel 20.0g (327.4mmol) of ethanolamine and 200mL of chloroform were added. 17.44g (163.7mmol) of vinyl chloroformate was added to the mixture over 20 minutes raising the temperature to 53° C. The reaction mixture was cooled to room temperature and stirred for 16 hours. The resolution precipitate was removed by filtration. The filtrate was evaporated to remove solvent and the residual oil was distilled (125° C ± 5C°, .89 Torr) to give 21.2g (161.7mmol, 98.8%) of a light yellow oil. FTIR (neat, capillary) 3314.69, 2940.08, 2885.15, 1705.86, 1648.26, 1522.62, 1458.28, 1432.05, 1403.96, 1363.49, 20 1339.67, 1294.21, 1244.90, 1160.44, 1116.66, 1059.67, 1010.44, 947.03, 921.01, 861.00, 768.57, 731.09, 1339.67, 1294.21, 1244.90, 1160.44, 1116.66, 1059.67, 1010.44, 947.03, 921.01, 861.00, 768.57, 731.09, 25 spectral analyses were consistent with the following chemical structure.



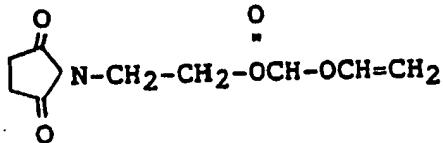
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1.2 N-(Vinyloxycarbonyloxy)-pyrrolidin-2,5-dione

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, and thermometer were added 10.0 (87.0mmol) of N-hydroxy succinimide, 6.9g (87.0mmol) of pyridine, and 100mL tetrahydrofuran was added. To the reaction mixture 9.25g (87.0mmol) of vinyl chloroformate was added so that the temperature remained below 10° C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl, and 100mL 2N NaOH. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting liquid chromatographed (silica gel, chloroform) to yield 10.0g (54.0mmol, 62.1% yield) of an oil. FTIR (neat, capillary) 3516.50, 3132.04, 3099.40, 3003.94, 2960.21, 1830.80, 1823.25, 1792.36, 1734.05, 40 1671.98, 1653.62, 1646.30, 1429.97, 1380.77, 1368.60, 1306.35, 1260.89, 1241.83, 1201.12, 1162.09, 1154.49, 1134.29, 1087.59, 1049.93, 1005.21, 990.18, 948.77, 941.86, 908.06, 897.29, 892.42, 812.37, 769.04, 756.85, 724.90, 707.81. NMR (CDCl_3) 6.73-7.09 (1H,q), 4.61-5.24 (2H,m), 2.78 (4H,s).

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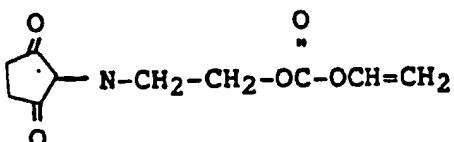
1.3 N-(Vinyloxycarbonyloxyethyl)pyrrolidin-2,5-dione

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To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, and thermometer were added 5.0 (35.0mmol) of N-(2-hydroxyethyl) succinimide, 2.8g (35.0mmol) of pyridine, and 100mL chloroform. To the reaction mixture was added 3.7g

(35.0mmol) of vinyl chloroformate so that the temperature remained below 10°C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2N NaOH. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting red liquid chromatographed (silica gel, chloroform). The recovered oil totaled 3.0g (14.1mmol, 40.2% yield). FTIR (neat, capillary) 1755.10, 1694.90, 1648.77, 1427.00, 1396.38, 1366.15, 1329.97, 1298.34, 1239.58, 1185.85, 1152.26, 1111.20, 1085.92, 1024.25, 1005.00, 946.53, 894.87, 882.46, 848.52, 818.51, 778.99, 700.00, 661.32. NMR (CDCl_3) δ 6.50-6.83 (1H,q), 4.13-4.66 (2H,m), 3.93-4.13 (2H,m), 3.33-3.66 (2H,m), 2.41 (4H,s).

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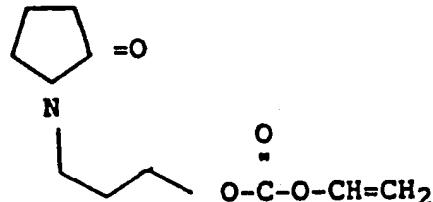
PART II - SYNTHESIS OF PYRROLIDINONE MOIETY CONTAINING MONOMERS

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2.0 3-(2-Pyrrolidinone-1-yl)propyl Vinyl Carbonate $C_{10}H_{15}NO_4$

To a 250mL 1-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, and ice bath, 12.5g (87.3mmol) of N-(3-hydroxypropyl)-2-pyrrolidinone, 7.6g (96.0mmol) of pyridine and 100mL of chloroform were added. To the ice cold reaction mixture 9.3g (87.3mmol) of vinyl chloroformate was added over 5 minutes. After 5 minutes a precipitate formed. The reaction mixture was adsorbed on silica gel then purified by chromatography (silica gel, methylene chloride) to give 17.3g (81.1mmol, 93.0%) of a straw colored oil. FTIR (neat, capillary) 2963.22, 1754.09, 1676.89, 1646.83, 1566.02, 1494.64, 1463.44, 1425.05, 1396.11, 1357.91, 1336.92, 1296.25, 1239.43, 1152.41, 1085.28, 1024.06, 998.00, 946.11, 882.00, 761.74, 737.53, 697.39, 651.25. NMR (CDCl_3) δ 6.82-7.17 (1H,m), 4.40-4.96 (2H,m), 4.06-4.28 (2H,m), 3.24-3.47 (4H,m), 1.68-2.56 (6H,m). The spectral analyses were consistent with the following chemical structure.

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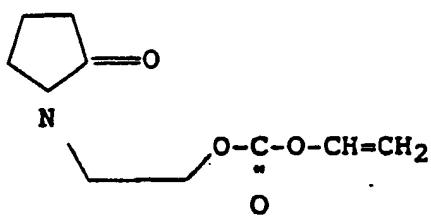


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2.1 2-(2-Pyrrolidinone-1-yl)ethyl Vinyl Carbonate $C_9H_{13}NO_3$

To a 250mL 1-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, and ice bath, were added 10.0g (77.4mmol) of N-2-(hydroxyethyl) pyrrolidinone, 6.7g (84.7mmol) of pyridine and 100mL of chloroform. To the ice cold solution 8.3g (78.0mmol) of vinyl chloroformate was added. The mixture was stirred for 30 minutes, forming a precipitate. The reaction mixture was chromatographed (silica gel, methylene chloride) 90% toluene 10% to give 8.3g (41.7mmol, 53.9%) of a light yellow oil. FTIR (neat, capillary) 2962.91, 1754.66, 1679.48, 1646.22, 1494.64, 1462.88, 1438.22, 1424.48, 1393.77, 1368.15, 1327.55, 1286.44, 1237.47, 1152.71, 1113.47, 1085.63, 1046.25, 1018.86, 979.70, 946.17, 894.98, 877.43, 853.32, 779.37, 735.01, 697.06, 650.86. NMR (CDCl_3) δ 6.84-7.17 (1H,m), 4.45-5.01 (2H,m), 4.18-4.35 (2H,m), 3.32-3.62 (4H,m), 1.70-2.50 (4H,m). Spectral analyses were consistent with the proposed chemical structure.



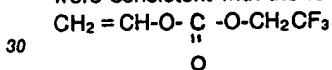
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PART III - SYNTHESIS OF HALOALKYL CONTAINING MONOMERS

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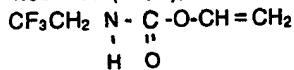
3.0 2,2,2-Trifluoroethyl Vinyl Carbonate C₅H₅O₃

To a 2 litre 4-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, thermometer, ice-water bath, and dropping funnel 47.45g (0.6 moles) of pyridine and 600mL of methylene chloride was added. The mixture was cooled to between 5° and 8°C, a white precipitate formed. Then 60.02g (0.6 moles) of 2,2,2-trifluoroethanol was added. The reaction was warmed to room temperature for 20 hours. A precipitate remained but had changed texture. The organics were washed thrice with 200mL 2N HCl, once with saturated NaCl then twice with 200mL 2N NaOH. The organics were dried over magnesium sulfate then distilled through an 8 inch vigreux to give a colorless oil which had the following characteristics (bp 107°C, 760.0 Torr), 66.1g (.389mole, 64.8%). FTIR (neat, capillary) 2985.97, 1790.03, 1653.80, 1447.48, 1412.48, 1386.07, 1316.41, 1255.45, 1185.52, 1157.41, 1098.83, 1082.16, 995.88, 962.47, 941.20, 910.72, 881.10, 777.15, 694.53, 665.95. NMR (CDCl_3) δ 6.88-7.26 (1H,m), 4.33-5.20 (4H,m). The spectral analyses were consistent with the following structure.



3.1 2,2,2-Trifluoroethyl Vinyl Carbamate C₅H₆F₃NO₂

To a 1L 3-neck round bottom flask fitted with a mechanical stirrer, condenser, thermometer, and ice water bath 32.11g (406.0mmol) of pyridine and 450mL of ether was added. After the temperature was stabilized at 12.5 °C ± 2.5 °C 21.6 203.0mmol of 2,2,2-trifluoroethyl amine hydrochloride was added in one portion, then the reaction was stirred to room temperature for 18 hours. The organics were washed twice with 300mL 2N HCl, once with 100mL 2N NaOH, then dried with magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was distilled at (70 °C, 30 Torr) to give a white crystalline solid (mp 43-44 °C) 6.8g (40.2mmol, 21.8%). FTIR (SRATR) 3325.47, 2957.22, 2921.47, 2852.61, 1722.84, 1651.46, 1540.06, 1458.41, 1427.89, 1396.91, 1299.01, 1281.24, 1237.54, 1150.23, 1121.40, 1023.84, 956.18, 946.33, 871.75, 830.76, 771.03, 669.23. NMR (CDCl_3) 6.95-7.27 (1H,m), 5.07-5.66 (1H,b), 4.33-4.86 (2H,m), 3.50-4.13 (2H,m).

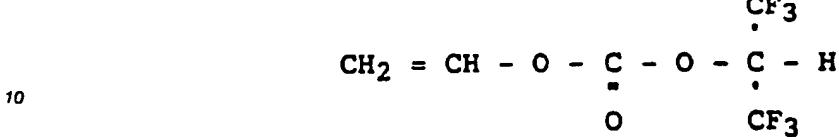


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3.2 1,1,1,3,3,3-Hexafluoroprop-2-yl Vinyl Carbonate C₆H₄F₆O₃

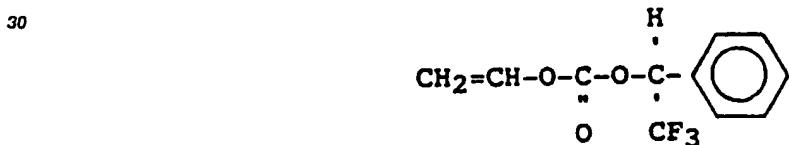
To a 1000mL 3-n ck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and ice-water bath 43.50g (550.0mmol) of pyridine and 600mL methylene chloride was added. After cooling to $5^{\circ}\text{C} \pm 2\text{C}$, 53.3g (500.0mmol) of vinyl chloroformate was added while maintaining the temperature. A white precipitate formed immediately. When the addition was complete, 92.4g (550.0mmol) 1,1,1,3,3,3-hexafluoro-2-propanol was added. The reaction was stirred at room temperature for 18 hours. The organics were washed twice with 500mL ice cold 2N HCl, once with 500mL ice-cold

saturated NaCl, dried over magnesium sulfate, and then distilled through an 8 inch vigreux to give a colorless oil (bp 97 °C, 760.0 Torr), 21.5g (90.3mmol, 18.1%). FTIR (neat, capillary) 2980.79, 1782.53, 1654.02, 1383.67, 1363.76, 1309.32, 1296.81, 1252.69, 1196.39, 1098.72, 1021.71, 936.52, 922.78, 905.85, 887.05, 866.80, 773.96, 712.08, 689.17. NMR (CDCl_3) δ 6.83-7.23 (1H,m), 5.26-5.86 (1H,m), 4.56-5.23 (2H,m).



15 3.3 2,2,2-Trifluoro-1-phenylethyl Vinyl Carbonate C₁₁H₉F₃O₃

To a 250mL round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, thermometer, ice-water bath, and dropping funnel 12.5g (71.0mmol) of 1-phenyl-2,2,2-trifluoroethanol, 7.6g (71.0mmol) triethylamine and 100mL ethylether was added. After cooling to 12.5 °C ± 3 °C, 7.6g (71.0mmol) of vinyl chloroformate was added while maintaining the temperature. The reaction mixture was filtered to remove triethylamine-hydrochloride. The filtrate was washed twice with 2N HCl, once with distilled water then dried with magnesium sulfate. The solvent was removed on a rotary evaporator and the crude oil was distilled to give a colorless oil (bp 90 °C, 4.5 Torr), 12.2g (49.6mmol, 69.8%). FTIR (neat, capillary) 1800.23, 1767.51, 1733.45, 1653.30, 1558.52, 1499.70, 1458.25, 1383.98, 1355.92, 1312.00, 1301.65, 1273.65, 1241.93, 1208.55, 1182.79, 1157.35, 1131.65, 1088.2, 1031.72, 998.12, 938.91, 928.82, 913.17, 877.34, 849.19, 776.46, 760.96, 696.97. NMR (CDCl_3) δ 7.30 (5H,S), 6.76-7.03 (1H,m), 5.66-6.00 (1H,m), 4.36-9.33 (2H,m).



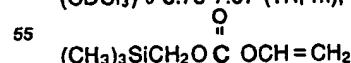
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PART IV - SILICON CONTAINING MONOMERS

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4.0 Trimethylsilylmethyl Vinyl Carbonate C₇H₁₄O₃Si

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, and thermometer was added 3.8g (48.0mmol) of pyridine then 50mL of chloroform. The mixture was cooled to 12 °C ± 3 °C with an ice-water bath. Next 5.0g (48.0mmol) of trimethylsilyl methanol then 5.1g (48.0mmol) of vinyl chloroformate were slowly added so that the temperature was maintained. The cooling bath was removed and the reaction mixture was stirred for one hour. The organics were washed four times with 100mL 2N HCl, twice with distilled water and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oil. The oil was passed through silica gel to give 4.8g (27.56mmol, 57.1%) of colorless oil. FTIR (neat, capillary) 2958.37, 1754.67, 1648.09, 1420.24, 1383.80, 1302.02, 1226.95, 1155.20, 1085.49, 944.10, 913.47, 840.69, 779.53, 735.78, 669.81, 668.88. NMR (CDCl_3) δ 6.73-7.07 (1H, m), 4.25-4.85 (2H,m), 3.73 (2H,S), 0.00 (9H,S).



4.1 Trimethylsilylvinyl Vinyl Carbonate C₈H₁₆O₃Si

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, and thermometer was added 6.69g (85.0mmol) of pyridine then 100mL of chloroform. The reaction was cooled to 12°C ± 3C° with an ice-water bath. Next 10.0g (85.0mmol) of trimethylsilyl ethanol and 9.01g (85.0mmol) of vinyl chloroformate were added so that the temperature was maintained. The cooling bath was removed and the reaction mixture was stirred for one hour. The organic phase was washed four times with 100mL 2N HCl, twice with distilled water then dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oil. The oil was passed through silica gel to give 6.0g (31.9mmol, 37.5%) of colorless oil. FTIR (neat, capillary) 2955.56, 1754.65, 1648.64, 1456.39, 1414.83, 1388.75, 1298.51, 1239.97, 1178.60, 1154.64, 1082.23, 1061.84, 1043.84, 1026.67, 943.56, 918.45, 856.41, 832.97, 784.30, 767.03, 694.35, 663.60. NMR (CDCl₃) δ 6.80-7.13 (1H,m), 4.42-4.91 (2H,m), 4.03-4.40 (2H,m), 0.87-1.15 (2H,m), 0.00 (9H,S).

O

15 (CH₃)₃SiCH₂CH₂O C OCH=CH₂

4.2 3-(Trimethylsilyl)propyl Vinyl Carbonate C₉H₁₈O₃Si

20 To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, and dropping funnel was added 25.0g (189mmol) of trimethylsilyl-3-propanol, 16.45g (208mmol) of pyridine and 175mL of toluene. In one portion, 22.1g (208mmol) of vinylchloroformate was added to the reaction mixture. An exotherm to 73°C was noted. The mixture was stirred for 3 hours at room temperature then at 50°C for 2 hours then at room temperature for 18 hours. The organic phase was washed with 250mL 2N HCl then with 250mL 2N NaOH₃ and the organic phase dried with magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil distilled to give a colorless oil (bp 115°C, 35 Torr), 14.7g (7.27mmol, 38.5%). FTIR (neat, capillary) 2955.00, 2898.21, 1758.60, 1649.23, 1468.16, 1453.00, 1439.73, 1414.72, 1391.72, 1350.50, 1298.51, 1239.70, 1190.91, 1157.19, 1090.25, 1057.10, 1031.32, 995.02, 944.19, 902.70, 856.58, 833.86, 782.42, 753.39, 691.98. NMR (CDCl₃) δ 6.86-7.18 (1H,m), 4.36-4.88 (2H,m), 3.96-4.18 (2H,m), 1.40-1.91 (2H,m), 0.36-0.65 (2H,m), 0.00 (9H,S).

30 CH₂=CH-O- C -O-CH₂CH₂CH₂Si(CH₃)₃

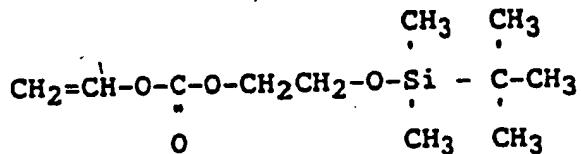
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4.3 t-Butyldimethylsiloxyethyl Vinyl Carbonate C₁₁H₂₂O₄Si

35 To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and ice-water bath was added 19.8g (112.3mmol) of tert-butyldimethylsiloxy ethyleneglycol, 9.8g (112.3mmol) of pyridine and 300mL of ether. After cooling to 10°C ± 5°C, 11.96g (112.3mmol) of vinyl chloroformate was added dropwise so that the temperature was maintained. A precipitate was formed and the reaction was stirred to room temperature over 16 hours. The organic phase was washed twice with 100mL 2NHCl, twice with 100mL 2N NaOH then dried over magnesium sulfate. The solvent was flashed off on a rotary evaporator and the resulting oil was passed through a short chromatography column (silica gel, chloroform) to give 26.9g (109.2mmol, 97.2%) of clear liquid. FTIR (neat, capillary) 2955.19, 2929.89, 2857.80, 1759.76, 1651.09, 1743.16, 1463.41, 1386.69, 1373.24, 1362.91, 1339.85, 1298.68, 1239.45, 1159.95, 1136.18, 1110.98, 1084.87, 1026.06, 1005.69, 944.16, 902.24, 869.65, 828.32, 812.16, 774.36, 714.82, 682.03, 661.17. NMR (CDCl₃) δ 6.78-7.12 (1H,m), 4.35-4.93 (2H,m), 4.03-4.26 (2H,m), 3.60-3.83 (2H,m) 0.82 (9H,S), 0.00 (6H,S).

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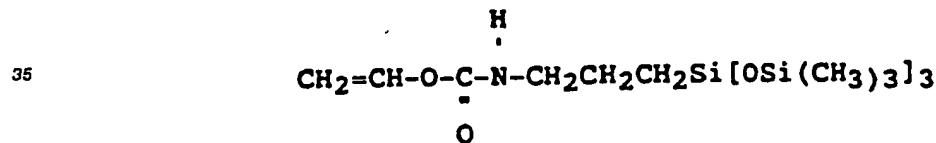
4.4 3-[Tris(trimethylsiloxy)silyl] propyl Vinyl Carbonate C₁₅H₃₆O₆Si₄

To a 100mL 3-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, thermometer, and condenser, was added 9.5g (38.0mmol) of 3-(trimethoxysilyl) propyl vinylcarbonate and 16.6g (125.3mmol) of trimethylsilylacetate. To this reaction mixture was added 3.45ml of a catalyst prepared by mixing 23.8g (242.7mmol) of sulfuric acid, 11.6g (251.8mmol) of absolute ethanol and 16.5g (916.0mmol) of water. The addition took twenty minutes and an 8°C exotherm was noted. The reaction was allowed to stir at room temperature for 16 hours and was then diluted with 200mL of chloroform, washed twice with 100mL 2N NaOH, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to give 15.3g of crude oil. Following chromatography (silica gel, 80% Heptane, 20% methylene chloride) the oil was distilled (bp 125 °C, 0.8 Torr), 3.5g (8.24 mmol, 21.7%). FTIR (neat, capillary) 2958.06, 2898.76, 1762.06, 1650.84, 1543.76, 1393.82, 1319.20, 1298.62, 1245.44, 1199.11, 1160.19, 1041.77, 975.14, 946.32, 833.42, 782.42, 753.08, 714.62, 686.73, 658.57. NMR (CDCl₃) δ 6.71-7.10 (1H,m), 4.28-4.83 (2H,m), 3.85-4.08 (2H,m), 1.36-1.85 (2H,m), 0.23-0.50 (2H,m), 0.00 (27H,S).

O
CH₂=CH-O-C¹-O-CH₂CH₂CH₂Si(OSi(CH₃)₃)₃

4.5 3-[Tris(trimethylsiloxy)silyl]propyl Vinyl Carbamate C₁₅H₁₇NO₅Si₄

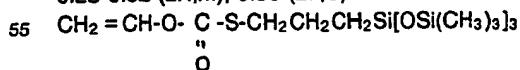
To a 100mL 3-neck round bottom flask fitted with a magnetic stirrer, and dropping funnel was added 5.0g (14.1mmol) of 3-amino propyl(trimethylsiloxy)silane, 1.23g (15.6mmol) of pyridine and 50mL of chloroform. Five minutes after adding 1.5g (14.1mmol) of vinyl chloroformate, an exotherm resulted. The reaction mixture was checked by gas chromatography after 10 minutes and the starting amine was consumed. The organic phase was washed once with 100mL 2N HCl then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford 5.8g of crude brown oil. Following chromatography (silica gel, 50% heptane 40% methylenechloride), 5.0g (11.8mmol, 83.3%) of colorless oil (bp 130 °C, .8 Torr) was obtained. FTIR (neat, capillary) 2957.80, 1751.43, 1718.38, 1648.64, 1529.69, 1445.45, 1407.29, 1293.71, 1249.76, 1195.93, 1165.08, 1041.17, 972.34, 951.33, 833.18, 752.97, 715.26, 686.34, 656.45. NMR (CDCl₃) δ 6.91-7.26 (1H,m), 4.16-4.66 (3H,m), 2.80-3.20 (2H,m), 1.20-1.71 (2H,m), 0.20-0.48 (2H,m), 0.00 (27H,S).



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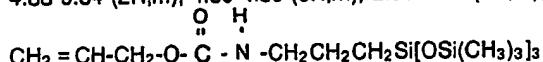
4.6 3-(Vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy) silane]

To a 500mL 1-neck round bottom flask fitted with a magnetic stirrer and a condenser, was added 33.0g (123.9mmol) of 3-(trimethoxysilyl) propyl thio vinyl carbonate and 81.9g (619.2mmol) of trimethyl silylacetate. With rapid stirring, 11.3mL of an acid catalyst prepared by mixing 23.8g (242.7mmol) of sulfuric acid, 11.6g (251.8mmol) of absolute ethanol and 16.5g (916.0mmol) of water) unsaturated. A vigorous exotherm was noted. After 30 minutes the reaction mixture was dissolved in 300mL chloroform and washed twice with 100mL of 2 N NaOH and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, chloroform). The product was distilled (160 °C, .8 Torr) to afford 25.5g (57.86mmol, 46.7%) of a colorless oil. FTIR (neat, capillary) 2957.71, 1720.75, 1645.91, 1250.16, 1136.24, 1113.53, 1098.48, 1038.97, 944.04, 912.93, 833.12, 751.61, 717.00, 686.49, 658.44. NMR (CDCl₃) δ 6.95-7.32 (1H,m), 4.32-4.85 (2H,m), 2.63-2.88 (2H,m), 1.62-1.88 (2H,m), 0.28-0.62 (2H,m), 0.00 (27,S).



4.7 3-[Tris(trimethylsiloxy)silyl]propyl Allyl Carbamate

To a 100mL 3-neck round bottom microware flask fitted with a magnetic stirrer, condenser, N₂ blanket, and dropping funnel, was added 4.8g (13.57mmol) of 3-aminopropyltris(trimethylsiloxy) silane, 1.18g (15.0mmol) of pyridine and 50mL of chloroform. To the reaction mixture, 1.65g (13.6mmol) of allyl chloroformate was added dropwise resulting in a pink color and an exotherm to near reflux. After 72 hours, the light yellow organic phase was washed once with 100mL 2N HCl, once with 100mL 2N NaOH, and then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford an oil. Following chromatography (silica gel, CHCl₃), the product was distilled (bp 123 °C, .7 Torr) to give 4.0g (9.1mmol, 66.6%) of a colorless oil. FTIR (neat, capillary) 2957.56, 1702.88, 1527.57, 1445.45, 1409.33, 1249.69, 1195.48, 1039.35, 993.11, 928.34, 833.37, 753.07, 717.02, 686.29, 656.22. NMR (CDCl₃) δ 5.52-6.13 (1H,m), 4.88-5.34 (2H,m), 4.36-4.80 (3H,m), 2.83-3.22 (2H,m), 1.16-2.00 (2H,m), 0.16-0.47 (2H,m), 0.00 (27H,S).

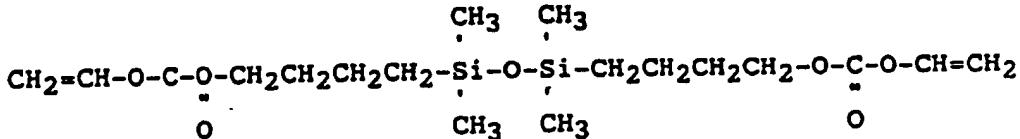


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4.8 1,3-Bis[4-(vinyloxycarbonyloxy)but-1-yl]-tetramethyl disiloxane

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N₂ blanket, dropping funnel, and thermometer, was added 10.0g (35.9mmol) of 1,3-bis (4-hydroxybutyl) tetramethylsiloxane, 6.24g (78.9mmol) of pyridine and 100mL of chloroform. Next, 7.64g (71.8mmol) of vinyl chloroformate was added to the mixture dropwise producing an exotherm to 54 °C. The reaction mixture was cooled to room temperature and stirred for 19 hours. The organic phase was washed twice with 100mL 2N HCl, twice with 100mL 2N NaOH, then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, chloroform) to give 13.22g (31.6mmol, 88.1%) of a light yellow oil. FTIR (neat, capillary) 2955.52, 1756.77, 1650.72, 1456.32, 1394.01, 1296.50, 1237.62, 1185.46, 1157.25, 1043.91, 990.80, 944.43, 868.86, 836.27, 781.65, 701.78. NMR (CDCl₃) δ 6.80-7.13 (2H,m), 4.37-4.92 (4H,m), 4.00-4.20 (4H,m), 1.55-1.88 (8H,m), 0.33-0.60 (4H,m), 0.00 (12H,S).

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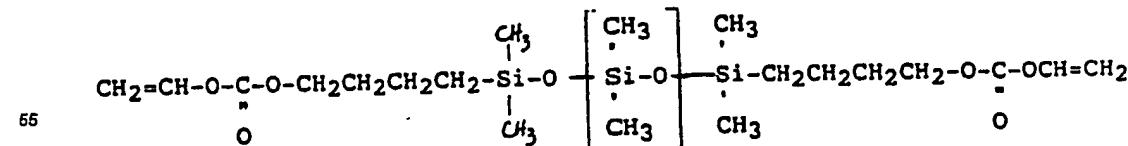


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4.9 "V₂D₂₅"

To a 100mL 1-neck round bottom microware flask fitted with a magnetic stirrer, and a drying tube was added 5.0g (11.95mmol) of 1,3-bis(4-vinyl butyl carbonate) tetramethyldisiloxane, 22.15g (74.7mmol) of octamethylcyclotetrasiloxane was added. Then 0.679g (0.452mmol) of trifluoromethanesulfonic acid was added to the reaction mixture. The reddish reaction mixture was stirred for 24 hours, then .38g (4.52mmol) of sodium bicarbonate was added which resulted in foaming. After 24 hours a small amount of black solids formed. The reaction mixture was filtered through 20.0g of activated F20 alumina to give a light yellow oil. The oil was heated at 80 °C at .25 Torr for 3 1/2 hours to remove volatiles, giving 13.4g (5.90mmol, 49.4%) of a light yellow oil. FTIR (neat, capillary) 2960.92, 1763.97, 1255.70, 1219.52, 1160.33, 1008.42, 946.68, 864.60, 782.03, 700.22, 686.57, 661.36. NMR (CDCl₃) δ 6.83-7.16 (2H,m), 4.36-4.93 (4H,m), 4.00-4.20 (4H,m), 1.16-1.91 (8H,m), .32-.62 (4H,m), 0.000 (168,S).

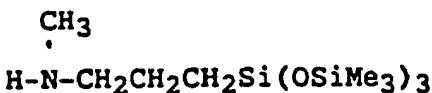
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4.10 -Methyl-N-[Tris(trimethylsiloxy)silylpropyl] vinyl carbamat

To a 300mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel was added 514.2g (3.186mmols) of hexamethyldisilazane. To the reaction flask was added 675mL of methanol over 30 minutes, when the addition was finished 75.0g (318.6mmol) of N-methyl-3-aminopropyltris(trimethoxy) silane was added. To the reaction was added 57.3g (3.186mmols) of distilled water. The reaction was stirred for 21 days and monitored by GC. During the 21 days 60.0g (3.33mmols) of water, 340mL methanol, and 228.0g (1.41mmols) of hexamethyldisilazane were added. The reaction mixture was reduced to 125.76g of crude oil by rotary evaporation. The crude material was distilled to give 62.6g (169.2mmol, 53.1%) of liquid N-methyl-3-aminopropyltris(trimethylsiloxy)silane bp. 64° 0.125mm Hg. FTIR (neat, capillary) 2957.80, 2899.02, 2790.57, 2361.73, 1471.38, 1443.26, 1412.16, 1343.04, 1249.97, 1218.84, 1187.71, 1083.76, 833.11, 751.60, 715.03, 686.34, 658.34. NMR (CDCl_3) 2.20-2.52 (2H,t), 2.24 (3H,s), 1.13-1.66 (2H,m), 0.99 (1H,s), 0.21-0.66 (2H,m), 0.00 (27H,s).

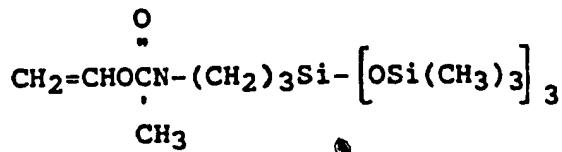
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To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer, ice-water bath was added 10.0g (27.2mmol) of N-methyl-3aminopropyltris(trimethylsiloxy) silane, 2.37g (30.0mmol) pyridine, and 200mL ether. Next was added 3.19g (30.0mmol) vinyl chloroformate so that the temperature remained below 15° C. After stirring for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2N NaOH, and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, methylene chloride). The product was recovered as an oil and was distilled (94-98° C, .1mm Hg) to yield 8.0g (18.3mmol, 67.2% yield). FTIR (neat, capillary) 2957.78, 2900.92, 1646.60, 1461.07, 1453.17, 1424.97, 1404.46, 1376.48, 1345.30, 1308.70, 1290.62, 1250.02, 1180.15, 1151.93, 1097.66, 1039.05, 952.11, 928.39, 833.42, 787.00, 753.10, 715.30. NMR (2H,t), 2.78 (3H,s), 1.20-1.70 (2H,m), 0.14-0.41 (2H,m), 0.00 (27H,s).

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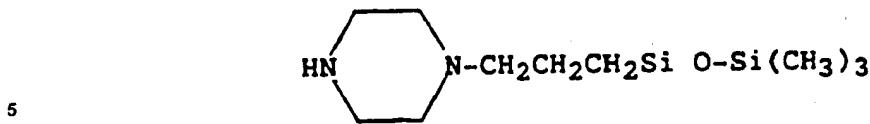


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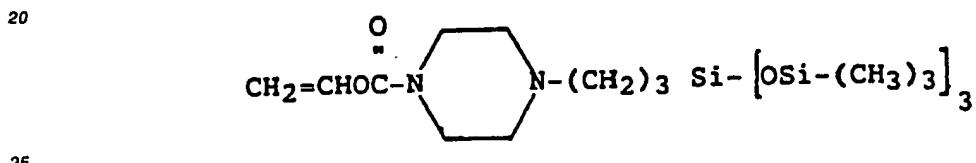
4.11 N-Vinyloxycarbonyl-N'-[tris(trimethylsiloxy)silylpropyl] piperazine

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, thermometer, oil bath was added 5.0g (58.0mmol) of piperazine and 230mL o-xylene. The reaction mixture was heated to $125 \pm 5^\circ$ and 11.0g (29.0mmol) of 3-chloropropyltris(trimethylsiloxy) silane was added dropwise. The reaction was heated for 48 hours, cooled, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was distilled to give the product 4.5g (10.7mmol, 18.4% yield). FTIR (neat, capillary) 3272.01, 2955.61, 2900.63, 2805.76, 2764.47, 2363.11, 1445.48, 1411.45, 1368.66, 1342.63, 1319.87, 1249.85, 1188.87, 1144.26, 1039.34, 833.42, 751.53, 712.61, 686.39, 656.40. NMR (CDCl_3) 3.60-3.93 (4H,m), 2.06-2.43 (6H,m), 1.66 (1H,s), 0.97-1.66 (2H,m), 0.12-0.40 (2H,m), 0.00 (27H,s).

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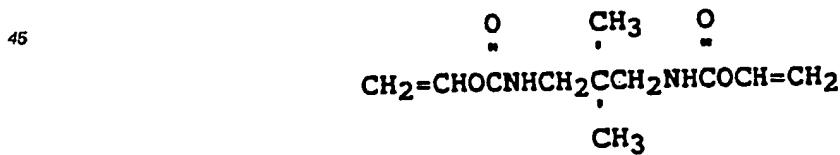


To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer and ice-water bath was added 5.0g (11.8mmol) of 3-tris(trimethylsiloxy)-
10 silylpropyl piperazine, .98g (12.4mmol) pyridine and 100mL ether. To the reaction mixture was added 1.32g (12.4mmol) vinyl chloroformate so that the temperature remained below 15°. After stirring for 18 hours the reaction mixture was washed with 100mL 2N HCl, 100mL 2N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, methylene chloride). The product was recovered as an oil 4.0g (8.1mmol, 68.8% yield).
15 FTIR (neat, capillary) 2957.40, 2900.69, 2808.30, 2770.50, 1646.32, 1460.48, 1429.87, 1373.46, 1353.45, 1334.61, 1291.27, 1249.73, 1227.01, 1187.92, 1152.02, 1100.89, 1039.50, 1000.33, 952.03, 833.45, 752.98, 712.79, 686.52, 656.44. NMR (CDCl₃) 6.89-7.30 (1H,dd), 4.28-4.76 (2H,m), 3.30-3.60 (2H,m), 2.13-2.40 (2H,m), 1.21-1.63 (2H,m), 0.17-0.63 (2H,m), 0.00 (27H,s).



4.12 2,2-Dimethyl N,N-bis(vinyloxycarbonyl)-1,3-propandiamine C₁₁H₁₈N₂O₄

30 To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, dropping funnel, and ice-water bath was added 15.5g (196.0mmol) of pyridine, 100mL of chloroform, 10.0g (98.0mmol) of 2,2-dimethyl-1,3-diamino propane. After cooling to 12.5 °C ± 2.5 °C, 20.8g (196.0mmol) of vinyl chloroformate was added so that the temperature was maintained. When the addition was completed, the reaction was stirred at room temperature for one hour. The organic phase was washed twice with 100mL 2N HCl, once with distilled water, twice with 2N NaOH, once with distilled water, once with 100mL 2N HCl, once with distilled water then was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, ethyl acetate) to afford a white solid (mp 92-98 °C), 14.4g (59.5mmol, 60.7%). FTIR 3356.25, 3330.18, 3101.77, 3091.71, 3047.38, 2967.99, 2962.39, 2932.08, 2875.70, 1733.54, 1725.58, 1710.82, 1676.99, 1649.18, 1527.92, 1473.90, 40 1458.90, 1440.71, 1394.41, 1371.29, 1360.72, 1299.03, 1257.64, 1244.48, 1201.55, 1157.95, 1106.46, 1062.40, 1025.93, 998.01, 979.97, 961.45, 951.57, 876.82, 866.36, 774.00, 720.42, 671.33. NMR (CDCl₃) 6.93-7.27 (2H,m), 5.46-5.93 (2H,s), 4.428-4.86 (4H,m), 2.83-3.10 (4H,d), 0.90 (6H,s).



4.13 N-(2-ethyl vinyl carbonate)-3-aminopropyltris(trimethylsiloxy) silane

55 To a 250mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, oil bath, thermometer was added 104.3g (1021.0mmol) 2,2-dimethyl-1,3-diaminopropane, 29.3g (79.0mmol) of 3-chloropropyltris (trimethylsiloxy) silane. The reaction was heated at 120 °C for 3

hours and stirred to room temperature for 24 hours. The reaction mixture was washed with 100mL 2N NaOH then the organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil distilled to give 23.8g (54.3mmol, 68.6% yield) bp 100°C. FTIR (neat, capillary) 2955.72, 2807.97, 2361.44, 1614.95, 1463.73, 1409.81, 1362.71, 1249.98, 1185.85, 1039.44, 833.64, 753.04, 714.78, 686.41, 657.85. NMR (CDCl_3) 2.25-2.56 (6H,m), 1.19-1.63 (2H,m), 1.06 (3H,s), 0.78 (6H,s), 0.07-0.45 (2H,m), 0.00 (27H,s).

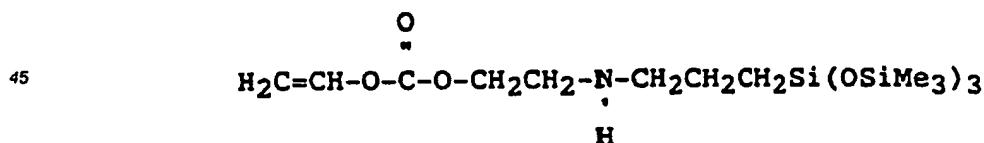
To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, ice-water bath, thermometer was added 6.3g (15.8mmol) N-(2-hydroxyethyl)-3-aminopropyltris(trimethylsiloxy) silane, 1.37g (17.4mmol) of pyridine, 100mL ether. To the reaction mixture was added 1.68g (15.8mmol) of vinyl chloroformate so that the temperature remained below 5°C.

After stirring to room temperature for 24 hours the reaction mixture was washed with 100mL 2N HCl then 100mL 2N NaOH then the organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 4.3g, chromatographed (silica gel, ethyl acetate 20% methylene chloride 80%). The oil recovered weighed 2.99g (6.4mmol, 25.4% yield). FTIR (neat, capillary) 2957.62, 2899.00, 1720.60, 1702.33, 1648.16, 1470.55, 1420.23, 1373.91, 1291.12, 1249.88, 1196.62, 1152.74, 1039.27, 951.52, 833.44, 753.18, 715.26, 686.53, 658.78. NMR (CDCl_3) 6.85-7.20 (1H,dd), 4.20-4.69 (2H,m), 3.36-3.71 (2H,bd), 3.00-3.36 (4H,m), 1.00-1.65 (2H,m), 0.09-0.40 (2H,m), 0.00 (27H,s).

20 4.14 3-[Tris(trimethylsiloxy)silyl]propylaminoethyl vinyl carbonate

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, oil bath and thermometer was added 100mL ethanolamine, 20.0g (53.5mmol) of 3-chloropropyltris(trimethylsiloxy) silane. The reaction was heated at 120°C for 4 hours then at 140°C for 1 hour. The reaction was cooled then diluted with 400mL distilled water then extracted twice with 100mL ether. The combined organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 23.0g, chromatographed (silica gel, gradient from 98.75% CH_2Cl_2 , 1.25% EtOAc to 100% MeOH) to give 6.6g (16.6mmol, 31.1%) FTIR (neat, capillary) 2957.55, 2898.62, 2834.28, 1453.19, 1411.46, 1249.92, 1191.11, 1039.00, 833.12, 751.49, 714.58, 686.18, 657.92. NMR (CDCl_3) 3.09-3.68 (4H,m), 2.25-2.43 (4H,m), 1.17-1.71 (2H,m), 0.07-0.47 (2H,m), 0.00 (27H,s).

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, ice-water bath and thermometer was added 6.3g (15.8mmol) N-(2-hydroxyethyl)-3-aminopropyltris(trimethylsiloxy) silane, 1.37g (17.4mmol) of pyridine and 100mL ether. To the reaction mixture was added 1.68g (15.8mmol) of vinyl chloroformate so that the temperature remained below 5°C. After stirring at room temperature for 24 hours the reaction mixture was washed with 100mL 2N HCl, 100mL 2N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 4.3g, chromatographed (silica gel, ethyl acetate 20% methylene chloride 80%). The oil recovered weighed 2.99g (6.4mmol, 25.4% yield). FTIR (neat, capillary) 2957.62, 2899.00, 1720.60, 1702.33, 1648.16, 1470.55, 1420.23, 1373.91, 1291.12, 1249.88, 1196.62, 1152.74, 1039.27, 951.52, 833.44, 753.18, 715.26, 686.53, 658.78. NMR (CDCl_3) 6.85-7.20 (1H,dd), 4.20-4.69 (2H,m), 3.36-3.71 (2H,bd), 3.00-3.36 (4H,m), 1.00-1.65 (2H,m), 0.09-0.40 (2H,m), 0.00 (27H,s).



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PART V - CYCLOALKYL AND CYCLOARYL CONTAINING MONOMERS

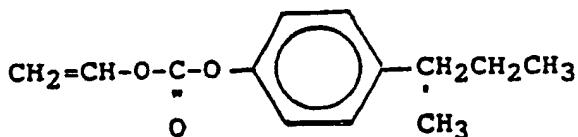
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5.0 4-s-Butylphenyl Vinyl Carbonate $\text{C}_{13}\text{H}_{16}\text{O}_3$

To a 250mL 1-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, ice-bath was

added 10.0g (66.6mmol) of 4-s-butylphenol, 5.8g (73.3mmol) of pyridine and 100mL of chloroform. To the stirred solution 7.08g (66.6mmol) of vinyl chloroformate was added over 5 minutes and the reaction mixture stirred for 30 minutes until pyridine hydrogen chloride precipitated. The organic phase was washed twice with 100mL of 2N HCl, dried over magnesium sulfate and the solvent removed on a rotary evaporator to give an oil. Following chromatography (silica gel, toluene), 9.6g (43.6mmol, 65.4%) of colorless oil was obtained. FTIR (neat, capillary) 2962.40, 2929.59, 2875.00, 1770.07, 1650.57, 1507.20, 1456.70, 1378.92, 1298.73, 1218.82, 1201.06, 1172.56, 1128.61, 1052.11, 1016.02, 997.93, 941.57, 913.17, 874.55, 835.99, 771.64, 730.98, 707.91, 696.57. NMR (CDCl_3) 7.08 (4H,S), 6.90-7.23 (1H,m), 4.50-5.10 (2H,m), 2.31-2.78 (1H,m), 1.33-1.81 (2H,m), 1.16-1.23 (2H,d), 0.68-1.00 (3H,m).

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20 5.1 4-t-Butylphenyl Vinyl Carbamate C₁₃H₁₇NO₂

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, ice water bath was added 7.1g (80.0mmol) of pyridine, 87.5mL of chloroform, 12.0g (80.0mmol) of 4-t-butylaniline. After cooling to 12.5 °C, 8.6g (80.0mmol) of vinyl chloroformate was added so that the temperature was maintained. When the addition is completed, reaction was stirred at room temperature for 3 hours. The organic phase was washed twice with 100mL 2N HCl, once with distilled water, twice with 2N NaOH, once with distilled water, once with 100mL 2N HCl, once with distilled water, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, CHCl_3) to give a white solid (mp 83-85 °C) 14.0g (65.1mmol, 81.4%). FTIR (KBr) 3317.67, 3248.14, 2960.58, 2903.46, 2868.29, 1718.64, 1649.04, 1615.15, 1600.07, 1543.48, 1476.36, 1460.81, 1412.07, 1363.76, 1324.04, 1301.85, 1270.05, 1244.76, 1152.47, 1123.96, 1113.56, 1064.50, 1016.24, 954.13, 858.83, 828.57, 744.72, 704.65, 681.65. NMR (CDCl_3) 7.27 (4H,S), 7.03-7.40 (1H,m), 6.64-6.82 (1H,S), 4.37-4.90 (2H,m), 1.27 (9H,S).

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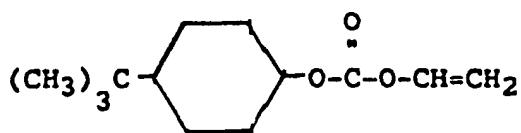


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5.2 4-t-Butylcyclohexyl Vinyl Carbonate

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, ice water bath, dropping funnel, was added 10.0g (64.0mmol) of 4-t-butylcyclohexanol, 5.6g (70.3mmol) of pyridine and 100mL of chloroform. The reaction mixture was cooled to less than 10 °C and 6.8g (64.0mmol) of vinyl chloroformate was added so that the temperature remained below 15 °C. The reaction mixture was stirred at room temperature for 20 hours, then washed with 100mL 2N HCl, 100mL distilled water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (silica gel, methylene chloride) to afford 7.3g (32.28mmol, 50.4%) of an oil. FTIR (neat, capillary) 2949.85, 2867.24, 1753.81, 1650.71, 1478.96, 1468.77, 1452.57, 1393.73, 1385.90, 1361.15, 1325.03, 1296.75, 1246.94, 1193.82, 1178.29, 1155.10, 1118.52, 1106.53, 1083.32, 1041.01, 1016.58, 1005.94, 946.14, 923.71, 902.63, 867.23, 843.74, 804.43, 783.98, 758.83, 696.74, 668.14. NMR (CDCl_3) 6.86-7.22 (1H,m), 4.37-4.97 (2H,m), 1.00-2.30 (10H,m), 0.85 (9H,S).

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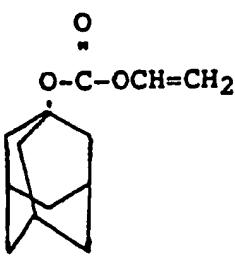
PART VI - ADDITIONAL MONOMER SYNTHESIS6.0 1-Adamantane vinyl carbonate

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To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 17.6g (116.0mmol) of 1-adamantanol, 9.3g (117.0mmol) of pyridine and 200mL chloroform. To the reaction mixture was added 12.5g (117.0mmol) of vinyl chloroformate so that the temperature remained below 10 degrees centigrade. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting white solid chromatographed (silica gel, chloroform). The white solid recovered 19.3g (86.4mmol, 74.5% yield) melting point 35-37 degrees centigrade. FTIR (KBr) 3430.92, 2914.51, 2855.03, 1756.33, 1651.33, 1458.19, 1321.61, 1312.23, 1296.45, 1246.83, 1160.25, 1103.75, 1082.53, 1041.68, 964.82, 892.90, 784.44. NMR (CDCl₃) 6.81-7.20 (1H,dd), 4.33-4.96 (2H,m), 1.50-2.40 (15H,m)

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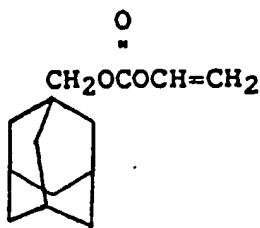
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6.1 1-Adamantanemethyl Vinyl Carbonate

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 10.0g (60.0mmol) of 1-adamantanemethanol, 4.8g (60.0mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 6.4g (60.0mmol) of vinyl chloroformate so that the temperature remained below 10 °C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid chromatographed (silica gel, chloroform). The white solid recovered totaled 12.0 (50.8mmol, 84.5% yield), melting point 44-45 °C. FTIR (KBr) 3423.04, 2906.49, 2580.27, 1759.74, 1649.15, 1391.84, 1322.44, 1260.77, 1231.42, 1190.53, 1147.22, 1087.78, 982.05, 951.64, 938.71, 889.75. NMR (CDCl₃) 6.89-7.27 (1H,dd), 4.40-5.05 (2H,m), 3.75 (2H,s), 1.43-2.13 (15H,m)

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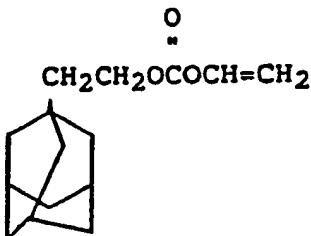
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6.2 1-Adamantane Vinyl Carbonate]

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, thermometer was added 5.0g (27.7mmol) of 1-adamanthanethanol, 2.2g (27.7mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 2.95g (28.0mmol) of vinyl chloroformate so that the temperature remained below 10 degrees centigrade. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (silica gel, chloroform). The oil recovered totaled 27.6g (10.8mmol, 38.5% yield). FTIR (neat, capillary) 2898.57, 2846.95, 1756.14, 1648.61, 1450.70, 1398.71, 1312.71, 1296.74, 1240.05, 1155.26, 1106.22, 1097.88, 1090.63, 975.27, 944.26, 933.77, 923.00, 900.75, 867.0, 782.34. NMR (CDCl_3) 6.86-7.20 (1H,dd), 4.38-4.92 (2H,m), 4.072-4.37 (2H,t), 1.33-2.18 (17H,m).

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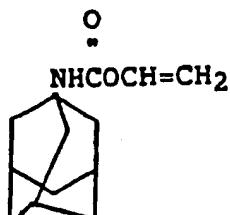
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6.3 1-Adamantane Vinyl Carbamate

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 10.0g (66.0mmol) of 1-adamantaneamine, 5.5g (70.0mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 7.4g (70.0mmol) of vinyl chloroformate so that the temperature remained below 10 °C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, chloroform). The tan solid totaled 5.2g (23.5mmol, 35.6% yield). FTIR (KBr) 3435.97, 3341.23, 2919.85, 2906.82, 2852.95, 1738.71, 1718.23, 1648.31, 1522.76, 1362.95, 1347.11, 1296.03, 1280.55, 1229.09, 1188.08, 1173.23, 1131.46, 1054.34, 1044.05, 952.14, 849.30. NMR (CDCl_3) 6.94-7.33 (1H,dd), 4.25-4.88 (3H,m), 1.56-2.26 (15H,m).

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6.4 N-(2-adamantyl)-O-2-Vinyloxycarbonylaminooethyl Carbamate

To a 250mL 3-neck round bottom flask that was fitted with a magnetic stirrer, condenser, nitrogen blanket, was added 6.33g (41.8mmol) of 2-adamantamine, 20.7g (41.8mmol) of 20% phosgene in toluene and 90mL of dry toluene. By means of a heating mantle the reaction was refluxed for eight hours, then allowed to cool to room temperature over night. To the reaction mixture was added 5.0g (38.0mmol) of 2-hydroxyethyl vinyl carbamate in 100mL of dry toluene. The reaction mixture was refluxed for eight hours then cooled to room temperature and the product was filtered and dried to give 5.4g (17.5mmol, 46.1% yield). FTIR (Kbr) 3320.53, 2911.77, 2854.81, 2708.48, 2622.82, 2587.66, 2530.60, 2062.48, 1710.68, 1648.47, 1625.62, 1604.50, 1594.43, 1514.68, 1476.34, 1453.03, 1403.83, 1363.71, 1348.91, 1323.96, 1311.38, 1295.64, 1250.12, 1185.17, 1111.58, 1056.19, 1012.80, 974.49, 949.05, 913.42, 863.76, 810.32, 769.55, 730.73, 694.94, 649.43. NMR (CDCl_3) 8.54-7.54 (2H,bs), 7.33-6.96 (1H,q), 4.85-4.26 (2H,m), 3.79-3.20 (4H,m), 2.33-1.33 (15H,m).

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6.5 N,N-dimethyl vinyl carbamate

To a 100mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, thermometer, fritted gas delivery tube, methanol-dry ice-bath was added 23.8g (223.4mmol) of vinyl chloroformate, 650mL of ether. When the reaction mixture was at -65 °C a stream of dimethylamine was added for 30 minutes. By gas chromatography the vinyl chloroformate was consumed. The reaction was stirred to room temperature over night. The organics were washed with 500mL distilled water then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil (20.3g) distilled to give 9.3g (80.8mmol, 36.2%). FTIR (neat, capillary) 3091.32, 2932.23, 1712.80, 1645.80, 1520.23, 1488.98, 1445.42, 1396.96, 1370.59, 1291.08, 1275.79, 1165.47, 1144.50, 1082.71, 1042.05, 951.61, 923.80, 859.37, 835.80, 758.66, 699.77, 681.97. NMR (CDCl_3) 7.02-7.33 (1H,q), 4.25-4.79 (2H,m), 2.92 (6H,s).

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6.6 N,N-diethyl vinyl carbamate

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel was added 3.2g (26.25mmol) of potassium t-butoxide, 50mL anhydrous tetrahydrofuran. After the solid was dissolved 5.6g (25.0mmol) of N,N-diethyl 2-bromoethyl carbamate was added and the reaction stirred for 30 minutes. To the reaction was added 100mL distilled water then the solvent was removed on the rotary evaporator. The residue was taken up in ether and filtered then distilled to give an oil 2.57g (17.9mmol, 71.8% yield). FTIR (neat, capillary) 2976.21, 2936.84, 2878.45, 1710.65, 1645.97, 1522.34, 1474.22, 1458.46, 1422.71, 1379.10, 1366.22, 1350.76, 1316.26, 1290.78, 1269.99, 1224.27, 1160.58, 1143.97, 1097.99, 1085.35, 1077.10, 1059.36, 987.36, 951.76, 858.41, 820.83, 781.32, 760.94, 699.54. NMR (CDCl_3) 7.07-7.39 (1H,q), 4.31-4.89 (2H,m), 3.12-3.46 (4H,q), 1.05-1.31 (6H,t).

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ADDITIONAL INTERMEDIATES

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2-Bromoethyl vinyl carbonate

To a 1L 4-neck round bottom flask fitted with a mechanical stirrer, thermometer, condenser, dropping funnel and nitrogen blanket was added 31.2g (250mmol) of 2-bromoethanol, 21.4g (270mmol) of pyridine and 400mL of ether. The reaction was cooled with an ice-water bath to less than 10 °C then 28.8g (270mmol) of vinyl chloroformate was added so that the temperature remained below 10 °C. The reaction was stirred to room temperature for 27 hours. Then the organics were washed twice with 2N HCl, twice with 2N NaOH, then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was passed through a short silica gel column, to remove most of the color, to give 38.4g (197mmol, 78.8% yield). FTIR (neat, capillary) 3672.76, 3469.03, 3096.75, 2972.97, 2155.40, 2057.14, 1754.37, 1648.44, 1563.96, 1455.87, 1443.36, 1427.17, 1388.17, 1299.17, 1285.60, 1244.29, 1221.29, 1152.23, 1095.86, 1049.38, 988.10, 940.93, 897.08, 875.78, 828.81, 778.74, 738.01, 694.54, 663.28. NMR (CDCl_3) 6.85-7.23 (1H,q), 4.40-5.10 (4H,m), 3.42-3.59 (2H,t).

N,N-diethyl-2-bromoethyl carbamate

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, thermometer, dropping funnel was added 19.3g (263.8mmol) of diethylamine and 250mL of dry toluene. To the reaction mixture was added 24.7g (131.9mmol) of 2-bromoethyl chloroformate. An exotherm to 40°C was noted along with the formation of a precipitate. After 1 hour at 70°C the organics were washed with 2N HCl then dried over magnesium sulfate. The solvent was removed on the rotary evaporator and the resulting oil distilled to give 6.5g (29.0mmol, 22% yield). FTIR (neat, capillary) 2973.85, 2934.58, 2875.90, 1692.95, 1478.36, 1458.21, 1422.49, 1379.09, 1365.61, 1350.53, 1314.77, 1267.60, 1224.49, 1164.67, 1093.11, 1075.29, 1003.67, 962.05, 948.43, 766.15, 647.29. NMR (CDCl_3) 4.23-4.49 (2H,t), 3.49-3.66 (2H,t), 3.10-3.52 (4H,q), 1.04-1.33 (6H,t).

PREFERRED CROSSLINKERS

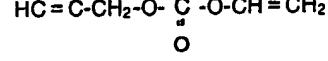
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PART VII - SYNTHESIS OF SIMPLE CROSSLINKERS

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7.0 Propargyl Vinyl Carbonate $\text{C}_6\text{H}_6\text{O}_3$

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and cooled within ice water bath was added 20.0g (356.8mmol) of propargyl alcohol, 31.0g (356.8mmol) of pyridine, 100mL of acetonitrile and 250mL of ether. After cooling to 5°C, 38.0g (356.8mmol) of vinyl chloroformate was added so that the temperature stayed below 10°C. The organic phase was washed with 400mL 2NHCl, 200mL 2N NaOH and dried with magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was passed through an 8 gram silica gel pad to afford a colorless oil 36.0g (285.5mmol, 80%). FTIR (neat, capillary) 3297.26, 1757.06, 1652.22, 1439.81, 1386.65, 1299.36, 1152.11, 1087.82, 1016.04, 984.84, 941.81, 915.98, 879.03, 779.08, 676.61, 663.07, 656.20. NMR (CDCl_3) 6.83-7.17 (1H,m), 4.43-5.05 (2H,m), 4.63-4.87 (2H,m), 2.46-2.60 (1H,m).



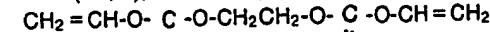
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PART VIII - OXYALKYLENE BRIDGED CROSSLINKERS

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8.0 1,2-bis-(Vinyloxycarbonyloxy)ethane

To a 100mL 3-neck round bottom microware flask fitted with a magnetic stirrer, condenser, N_2 blanket, and dropping funnel was added 5.0g (81.6mmol) of ethylene glycol, 12.8g (163.0mmol) of pyridine and 50mL of chloroform. To the reaction mixture, 17.38g (163.2mmol) of vinyl chloroformate was added over 5 minutes. The black reaction mixture was stirred at room temperature for 72 hours. The reaction mixture was washed once with 100mL 2N HCl, once with 100mL 2N NaOH and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (silica gel, chloroform). The product was distilled (110°C, 5 Torr) to afford 6.5g (32.2mmol, 39.4%) of a colorless oil. FTIR (neat, capillary) 1752.03, 1648.58, 1455.73, 1445.68, 1406.42, 1386.28, 1373.53, 1345.23, 1301.17, 1268.47, 1221.46, 1152.52, 1080.66, 1028.57, 1007.91, 941.86, 903.05, 866.96, 777.05, 696.37. NMR (CDCl_3) δ 6.85-7.18 (2H,m), 4.52-5.04 (4H,m), 4.40 (4H,S).

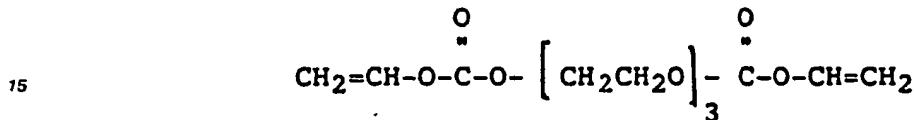


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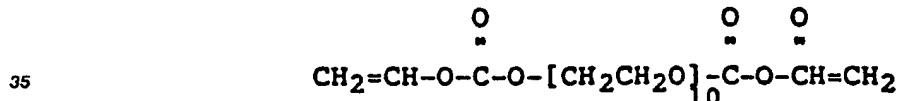
8.1 α,ω -bis-(Vinyloxycarbonyl)triethyl neglycol C₁₂H₁₈O₈

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, and dropping funnel was added 10.0g (66.6mmol) of triethyleneglycol, 5.79g (73.3mmol) of pyridine and 100mL of chloroform. Next, was added 7.80g (73.3mmol) of vinyl chloroformate, an exotherm was noted and the reaction mixture was stirred at room temperature for 18 hours. The organic phase was washed twice with 100mL 2N HCl, twice with 100mL 2N NaOH and dried with magnesium sulfate. The solvent was removed on a rotary evaporator to give an oil that was chromatographed (silica gel, CHCl_3) to afford an oil 2.6g (8.9mmol, 13.5%). FTIR (neat, capillary) 2959.95, 2877.99, 1752.00, 1648.22, 1453.36, 1388.35, 1368.46, 1355.89, 1337.65, 1298.80, 1234.17, 1152.82, 1082.40, 1023.62, 943.56, 902.67, 869.75, 779.08, 697.03. NMR (CDCl_3) 6.98-7.63 (2H,m), 4.40-5.03 (4H,m), 4.20-4.40 (4H,m), 3.60-3.80 (4H,m).



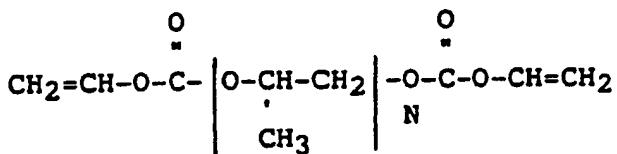
20 8.2 α,ω -bis-(Vinyloxycarbonyl)polyethylene Glycol C₂₆H₄₆O₁₅

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, and dropping funnel was added 10.0g (16.6mmol) of poly(ethyleneglycol), 3.2g (36.5mmol) of pyridine and 200mL of chloroform. Next, 3.9g (36.5mmol) of vinyl chloroformate in 5mL chloroform was added. A slight exotherm to 30 °C was noted. The reaction was stirred at room temperature for 48 hours and the organic phase washed twice with 100mL 2N HCl, twice with 100mL 2NaOH, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, CHCl₃) to afford 1.3g (2.17mmol, 13.0%) of colorless oil. FTIR (neat, capillary) 2867.87, 1756.21, 1648.17, 1455.18, 1388.46, 1350.26, 1298.44, 1247.57, 1083.45, 1026.37, 944.30, 871.74, 781.69. NMR (CDCl₃) 6.85-7.17 (2H,m), 4.34-5.00 (4H,m), 3.60-4.35 (40H,m).



40 8.3 α,ω -bis(Vinyloxycarbonyl) Polypropylene Glycol (mw approx. 1000)

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 20.0g (47.0mmol) polypropylene glycol (mw 1000) 7.6g (96.0mmol) of pyridine and 200mL chloroform. To the reaction mixture was added 10.2g (96.0mmol) of vinyl chloroformate so that the temperature remained below 10 degrees centigrade. After stirring at room temperature for 48 hours the reaction mixture was washed with 100mL 2N HCl, 100mL 2 N NaOH and the organic phase dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (short column silica gel, chloroform). The oil recovered weighed 14.6g (25.9mmol, 55.0% yield). FTIR (neat, capillary) 3096.15, 2973.01, 2934.02, 2870.93, 2335.49, 1754.56, 1648.30, 1568.82, 1453.53, 1375.64, 1349.76, 1296.84, 1249.99, 1152.61, 1083.39, 1051.95, 1018.85, 944.06, 923.43, 908.46, 868.85, 783.82, 697.48, 668.50. NMR (CDCl_3) 6.86-7.23 (2H, dd), 4.61-5.06 (4H,m), 3.33-3.76 (2H,m), 1.03-1.43 (2H,m).



Where N is an average value that gives the polypropylene glycol moiety an average molecular weight of about 1000.

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8.4 α,ω -Bis(Vinyloxycarbonyl)polyethylene Glycol mw approx. 1000

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 20.0g (20.0mmol) polyethylene glycol (mw 1000), 3.5g (44.0mmol) of pyridine, 200mL chloroform. To the reaction mixture was added 4.7g (44.0mmol) of vinyl chloroformate so that the temperature remained below 10 °C. After stirring at room temperature for 48 hours the reaction mixture was washed with 100mL 2 N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting low melting solid weighed 18.0g (16.0mmol, 79.9% yield). FTIR (neat, capillary) 3477.73, 2868.36, 2360.96, 1959.64, 1758.88, 1725.44, 1648.24, 1465.99, 1453.61, 1388.65, 1358.03, 1342.58, 1298.64, 1255.02, 1142.06, 1100.49, 1060.10, 944.47, 872.48, 841.08, 782.12, 756.09, 730.85, 699.44. NMR (CDCl_3) δ 6.83-7.20 (2H,dd), 4.40-4.96 (4H,m), 3.58 (88H,s).

25 $\text{CH}_2=\text{CHO}\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{CH}_2\text{CH}_2\text{O})_N\overset{\text{O}}{\underset{\text{H}}{\text{C}}}\text{OCH}=\text{CH}_2$
Where N is an average value that gives the polyethylene glycol moiety an average molecular weight of about 1000.

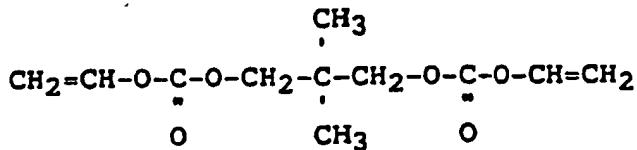
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PART IX - SYNTHESIS OF BRANCHED ALKYL BRIDGED CROSSLINKERS

9.0 2,2-Dimethyl-1,3-bis-(Vinyloxycarbonyloxy)propane

35 To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, ice-water bath, and dropping funnel was added 20.0g (192.0mmol) of 2,2-dimethyl-1,3-propanediol, 16.7g (211.2mmol) of pyridine and 200mL of chloroform. To the reaction mixture was added 20.45g (192.0mmol) of vinyl chloroformate was added over 20 minutes. After 1 hour, the reaction was allowed to warm to room temperature for 20 hours. The organic phase was washed twice with 100mL 2 N HCl, twice with 100mL 2 N NaOH and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator to afford an oil. Following chromatography (silica gel, 80% heptane, 20% methylene chloride) 6.4g (26.2mmol, 13.6%) of colorless oil was obtained. FTIR (neat, capillary) 2970.57, 1754.14, 1650.67, 1568.46, 1540.34, 1476.77, 1406.71, 1386.46, 1375.68, 1299.22, 1227.23, 1152.73, 1085.68, 1054.54, 1020.91, 961.81, 941.38, 871.66, 779.08, 696.42. NMR (CDCl_3) δ 6.80-7.18 (1H,m), 4.45-4.98 (2H,m), 3.98 (4H,S), 1.04 (6H,S).

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9.1 N,O-bis-(Vinyloxycarbonyl)ethanolamine $\text{C}_8\text{H}_{11}\text{O}_5$

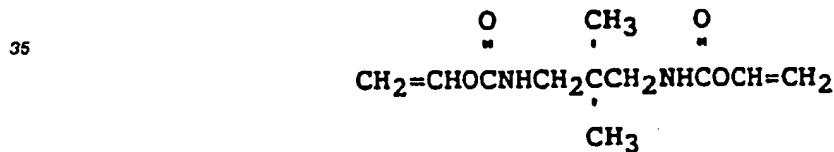
To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen

blanket, dropping funnel and an ice-water bath was added 27.2g (344.0mmol) of pyridine, 10.0g (164.0mmol) of aminoethanol and 100mL of ether. Next, 36.7g (344.0mmol) of vinyl chloroformate was added so that the temperature remained below 15 °C. The reaction was stirred at room temperature for 72 hours and 50mL acetonitril and 5.0g (50.0mmol) of vinyl chloroformate were added. The mixture was 5 stirred 24 hours and the organic phase washed thrice with 100mL 2N HCl, twice with 100mL distilled water, thrice with 100mL 2N NaOH, twice with 100mL distilled water, once with 100mL 2N HCl, once with 100mL distilled water and then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to give a solid which was chromatographed (silica gel, CHCl_3) recrystallized (toluene: heptane, 2:8) to afford a white solid (mp 45-46 °C), 9.4g (46.7mmol, 27.2%). FTIR (KBr) 3507.66, 3318.44, 3124.82, 3047.20, 10 2998.82, 2967.94, 2952.25, 2849.60, 2754.60, 1761.20, 1734.02, 1707.59, 1679.14, 1650.91, 1540.99, 1465.42, 1433.12, 1399.05, 1383.81, 1368.76, 1306.65, 1275.59, 1173.28, 1156.81, 1116.49, 1088.57, 15 1033.54, 1008.11, 964.70, 948.83, 928.54, 902.88, 887.36, 877.39, 850.91, 782.45, 699.45, 699.43. NMR (CDCl_3) 6.83-7.32 (1H,m), 5.06-5.43 (1H,S), 4.37-5.06 (2H,m), 4.27-4.36 (2H,m), 3.30-3.70 (2H,m).

15 $\text{CH}_2 = \text{CHO} \begin{array}{c} \text{O} \\ | \\ \text{C} \end{array} \text{NHCH}_2\text{CH}_2\text{O} \begin{array}{c} \text{O} \\ | \\ \text{C} \end{array} \text{OCH} = \text{CH}_2$

9.2 2,2-Dimethyl-N,N-bis(vinyloxycarbonyl)-1,3-propanediamine C₁₁H₁₈N₂O₄

20 To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, dropping funnel, and ice-water bath was added 15.5g (196.0mmol) of pyridine, 100mL of chloroform and 10.0g (98.0mmol) of 2,2-dimethyl-1,3-diaminopropane. After cooling to 12.5 °C ± 2.5 °C, 20.8g (196.0mmol) of vinyl chloroformate was added so that the temperature was maintained. When the addition was complete, the reaction was stirred at room temperature one hour. The organic phase was washed twice 25 with 100mL 2N HCl, once with distilled water, twice with 2N NaOH, once with distilled water, once with 100mL 2N HCl, once with distilled water and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, ethyl acetate) to afford a white solid (mp 92-98 °C), 14.4g (59.5mmol, 60.7%). FTIR 3356.25, 3330.18, 3101.77, 3091.71, 3047.38, 2967.99, 2962.39, 2932.08, 2875.70, 1733.54, 1725.58, 1710.82, 1676.99, 1649.18, 1527.92, 1473.90, 30 1458.90, 1440.71, 1394.41, 1371.29, 1360.72, 1299.03, 1257.64, 1244.48, 1201.55, 1157.95, 1108.46, 1062.40, 1025.93, 998.01, 979.97, 961.45, 951.57, 876.82, 866.36, 774.00, 720.42, 671.33. NMR (CDCl_3) 6.93-7.27 (2H,m), 5.46-5.93 (2H,S), 4.428-4.86 (4H,m), 2.83-3.10 (4H,d), 0.90 (6H,S).



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9.3 1,6-divinylhexylidicarbamate

45 To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer was added 5.0g (43mmol) of 1,6 diaminohexane, 7.12g (90mmol) of pyridine, 100mL anhydrous acetonitrile, 100mL ether. After the starting material was dissolved 9.26g (87mmol) of vinyl chloroformate was added over 20 minutes an exotherm was noted, and a precipitate formed over 18 hours. The solvent was removed on a rotary evaporator and the residue was dissolved in methylene 50 chloride, washed with 2N NaOH, thrice with distilled water then dried with magnesium sulfate. The solid was coated on silica gel and chromatographed (97% CH_2Cl_2 , 3% ETOAc) to give a solid that was dissolved in methylene chloride and slowly added to stirred heptane. The solid recovered was dried to give 5.7g (22.2mmol, 51.7% yield) melting point 94-98 °C. FTIR 3333.74, 3086.01, 3032.62, 2947.83, 2886.20, 2857.98, 1713.28, 1682.02, 1648.85, 1528.09, 1476.87, 1465.92, 1339.48, 1294.01, 1259.77, 1224.55, 55 1156.32, 1051.88, 1001.10, 954.5, 875.05, 866.57. NMR (CDCl_3) 7.00-7.34 (2H,q) 4.62-5.13 (2H,bs), 4.29-4.75 (4H,m), 2.91-3.33 (4H,q), 1.31 (8H,bs).

9.4 1,8-divinyloctyldicarbamate

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer was added 5.0g (34.6mmol) of 1,8 diaminoctane, 6.1g (76.1mmol) of pyridine, 100mL anhydrous acetonitrile, 100mL ether. After the starting material was dissolved 8.0g (87mmol) of vinyl chloroformate was added over 20 minutes an exotherm was noted, and a precipitate formed over 18 hours. The solvent was removed on a rotary evaporator and the residue was dissolved in methylene chloride, washed with 2N NaOH, thrice with distilled water then dried with magnesium sulfate. The solid was coated on silica gel and chromatographed (97% CH_2Cl_2 , 3% ETOAc) to give a solid that was dissolved in methylene chloride and slowly added to stirred heptane. The solid recovered was dried to give 6.7g (22.1mmol, 64.1% yield) melting point 83-88 °C. FTIR 3336.20, 3086.75, 3032.18, 2996.55, 2942.19, 2926.73, 2872.60, 2855.14, 1709.82, 1676.68, 1649.06, 1530.29, 1478.71, 1464.03, 1362.59, 1308.80, 1257.38, 1252.87, 1213.85, 1168.05, 1083.04, 1062.73, 1031.76, 956.24, 874.73, 861.46. NMR (CDCl_3) δ 6.95-7.34 (2H,q), 4.62-5.13 (2H,bs), 4.29-4.75 (4H,m), 2.97-3.30 (4H,q), 1.31 (10H,bs).

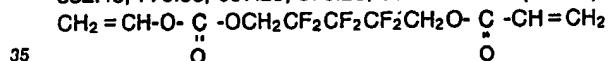
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PART X - FLUOROALKYL BRIDGED CROSSLINKERS

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10.0 1,5-bis-(Vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane $\text{C}_{11}\text{H}_{10}\text{F}_6\text{O}_5$

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and ice-water bath was added 12.3g (155.5mmol) of pyridine and 200mL of methylene chloride. After cooling to 5 °C ± 2°C add 16.57g (155.5mmol) of vinyl chloroformate was added so that the temperature was maintained. A white precipitate formed immediately. When the addition was complete, 15.0g (70.7mmol) of 2,2,3,3,4,4-hexafluoro-1,5-pentaneidiol in one portion as a slurry with 250mL methylene chloride was added. The reaction was allowed to warm to room temperature for 18 hours. The organics were washed twice with 250mL of 2N HCl then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford 24.7g of a straw oil. Following chromatography (silica gel, toluene), 21.8g (61.9mmol, 87.6%) of colorless oil was obtained. FTIR (neat, capillary) 3102.29, 2983.43, 1767.41, 1651.43, 1442.83, 1404.75, 1303.52, 1247.26, 1151.88, 1125.91, 1095.64, 1031.24, 1005.65, 985.71, 939.37, 882.43, 776.53, 697.20, 673.23, 650.18. NMR (CDCl_3) δ 6.83-7.26 (2H,m), 4.30-5.23 (8H,m).



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COPOLYMER FILM EXAMPLES

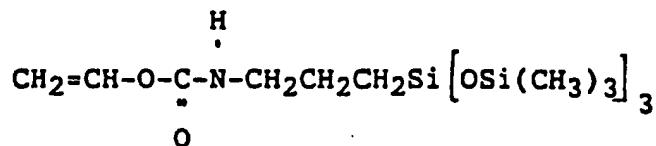
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A. HYDROGEL MATERIALS

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Soft hydrogel copolymers of the present invention were produced by copolymerizing a monomer of the formula

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with N-vinylpyrrolidinone (NVP), and the crosslinker monomer 1,5-bis-(vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane, in the presence of a nonreactive diluent and a UV irradiation, free radical initiator in the following weight ratios:

film #	hydrophilic monomer	NVP	X-linkers	%H ₂ O	DKx10 ⁻¹¹
5	1	22.5	65.0	2.5	73
	2	62.5	25.0	2.5	19
	3	64.5	24.7	0.5	25
	4	23.5	45.0	1.5	63
	5	53.5	25.0	1.5	27
10	6	42.5	25.0	2.5	33
	7	2.5	65.0	2.5	85
	8	23.5	65.0	1.5	77
	9	44.5	45.0	0.5	58
	10	21.5	64.7	0.9	80
15	11	43.1	43.1	0.9	53
	12	64.7	21.5	0.9	23
	13	32.5	45.0	2.5	51
					37

These films were prepared by placing the prepolymer mixtures between glass plates separated by a Teflon® peripheral gasket and were UV irradiated for 2 hours. The samples were then prepared for physical characterization.

Physical properties for films were determined using the following test procedures:

1. Tensile strength (g/mm²) and modulus of elasticity were measured per ASTM test method D1708.
2. Elongation was measured per ASTM 1708.
3. Initial tear strength and propagation tear strength were measured per ASTM 1438.
4. Oxygen permeabilities were measured by the method reported by Relojo, M. et al in Contact and Intraocular Lens Medical Journal, Vol. 3, issued p. 27 (1977) and edge effects were accounted for per the methods described by Fatt, et al. in International Contact Lens Clinic, v. 14, p. 389 (1987).
5. Water content is measured per a gravimetric method.
6. Refractive index was measured per typical methods on hydrated samples using a refractometer.

The physical characterization of these films is reported in the following table.

Film	Modulus (g/mm ²)	Tensile (g/mm ²)	Elongation %	Tear (initial/propagation) (g/mm ²)
40	1	38	15	60
	2	970	170	130
	3	203	77	330
	4	52	28	70
	5	370	100	160
45	6	262	72	90
	7	27	7	42
	8	17	13	120
	9	18	20	280
	10	72	43	75
50	11	49	27	180
	12	430	110	200
	13	86	40	70
				3.2/3.1

As can be seen, all of the above film samples meet the general requirements for a hydrogel contact lens material.

B. HARD CONTACT LENS MATERIAL EXAMPLES

Hard, gas permeable contact lens materials were made using the novel vinylcarbonate functional monomers described herein by polymerizing 1,1,1,3,3,3-hexafluoroprop-2-yl vinyl carbonate (hfpcv)



¹⁰ with a variety of hydrophilic monomers and crosslinkers, such as those known in the prior art and the preferred hydrophilic monomers and crosslinkers disclosed herein.

Other materials can be made by substituting the 1,1,1,3,3-hexafluoroprop-2-yl vinyl carbonate monomer with a fluoroalkyvinyl carbonate or carbamate monomer preferably chosen from the group consisting of trifluoroethyl vinyl carbonate (tfevc); 1,5-bis-(Vinylxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane (hfpdvc); and 2,2-trifluoro-1-phenylethyl Vinyl carbonate (tfvvc).

Films were made by the general method described in the hydrogel film example. The films were polymerized from monomer mixtures with the following formulations.

polymerized were measured. Examples include the following:
 20 film #14: 65 wt% hfpvc
 30 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 5 wt% hpdvc and about
 0.5 wt% free radical initiator
 film #15: 65 wt% hfpvc
 30 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate and
 25 0.5 wt% free radical initiator
 film #16: 65 wt% hfpvc
 30 wt% 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbamate
 4.0 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 0.5 wt% free radical initiator
 30 film #17: 60 wt% hfpvc
 25 wt% 3[tris(trimethylsiloxy)silyl] propyl vinyl carbonate
 5 wt% V₂ D₂₅
 5 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 5 wt% N-vinyl-2-pyrrolidinone
 35 0.5 wt% free radical initiator
 film #18: 60 wt% hfpvc
 25 wt% 3[tris(trimethylsiloxy)silyl]propyl vinyl carbonate
 5 wt% V₂ D₂₅
 5 wt% hpdvc
 40 5 wt% N-vinyl-2-pyrrolidinone
 0.5 wt% free radical initiator
 film #19: 60 wt% hfpvc
 25 wt% 3-(vinyloxycarbonylthio)propyl-[tris (trimethylsiloxy)silyl]propylsilane allylcarbamate
 5 wt% V₂ D₂₅
 45 5 wt% hpdvc
 5 wt% N-vinyl-2-pyrrolidinone
 0.5 wt% free radical initiator
 film #20: 60 wt% hfpvc
 25 wt% 3-tris(trimethylsiloxy) propylsilane allylcarbamate
 50 5 wt% V₂ D₂₅
 5 wt% 2,2,3,3,4,4-hexafluoro-1,5-pentane dinvinylcarbonate
 5 wt% N-vinyl-2-pyrrolidinone
 0.5 wt% free radical initiator

The physical characteristics of these films as measured are reported in the following table.

	film #	modulus (g/mm ²)	tensile (g/mm ²)	% elongation	O2 Perm x 10 ⁻¹¹
5	14	75000	1250	14	130
	15	82000	1500	13	140
	16	80000	2100	8	130
	17	73000	2000	8	120
	18	85000	1600	16	130
	19	84000	1800	7	100
10	20	101000	2500	7	100

All of these films are acceptable as hard gas permeable contact lens materials.

15

C. SOFT NON-HYDROGEL MATERIAL EXAMPLES

- A series of films were made by the general film casting technique described in the hydrogel materials example except that prepolymer mixtures for the various films were employed as hereinafter disclosed.
- 20 film #21: 50 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 35 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10 wt% N-vinyl-2-pyrrolidinone
 5 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 25 0.5 wt% UV free radical initiator
 film #22: 25 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 64 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 30 0.5 wt% UV free radical initiator
 film #23: 44 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 44 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10.5 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 35 0.5 wt% UV free radical initiator
 film #24: 54 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 35 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 40 0.5 wt% UV free radical initiator
 film #25: 65 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 25 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 45 0.5 wt% UV free radical initiator
 film #26: 40 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 40 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 20 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 50 0.5 wt% UV free radical initiator
 film #27: 34 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 34 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 30 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane
 55 0.5 wt% UV free radical initiator
 film #28: 28 wt% 3-(trimethylsilyl)propyl vinyl carbonate
 68 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 4 wt% N-vinyl-2-pyrrolidinone

- 1 wt% 2,2-dimethyl-1,3-(vinyloxycarbonyloxy)propane
 0.5 wt% UV free radical initiator
 film #29: 20 wt% trimethylsilylmethyl vinyl carbonate
 70 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 5 10 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-(vinyloxycarbonyloxy)propane
 0.5 wt% free radical initiator
 film #30: 20 wt% trimethylsilylethyl vinyl carbonate 70 wt% 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate
 10 10 wt% N-vinyl-2-pyrrolidinone
 1 wt% 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy) propane
 0.5 wt% free radical initiator

The films were cured, samples were taken of the film and the following characteristics measured:

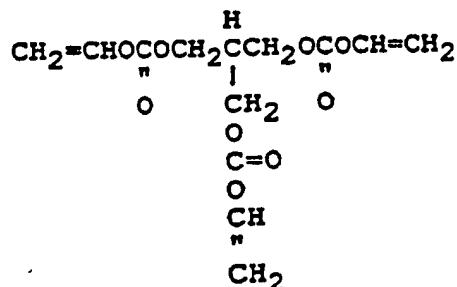
	film #	modulus (g/mm ²)	tensile strength (g/mm ²)	% elongation	Tear Strength (initial/propagation)	O ₂ DKx10 ⁻¹¹
20	21	2200	440	106	120/120	76
	22	270	150	234	80/80	140
	23	143	140	266	70/70	100
	24	120	140	270	70/70	90
	25	110	120	270	80/80	72
25	26	35	40	210	14/14	56
	27	50	70	290	30/30	80
	28	400	120	200	100/100	110
	29	—	—	—	—	100
	30	—	—	—	—	100

30 The above sample films demonstrated characteristics which would be useful as a soft, elastomeric, contact lens material with low or no water content.

35 1,2,3-tris(vinyloxycarbonyloxy) propane

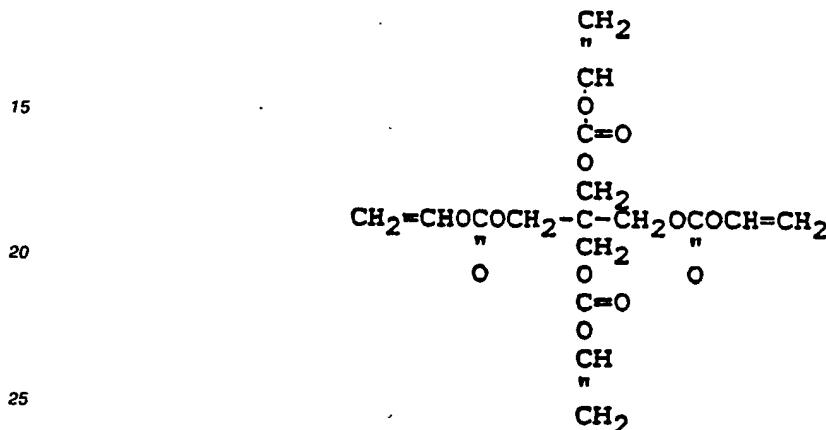
To a 250mL three neck round bottom flask fitted with a mechanical stirrer, condensor, nitrogen blanket, and a dropping funnel was added 3.1g (33.7mmol) of glycerol, 8.7g (110mmol) of pyridine and 125mL of anhydrous acetonitrile. The reaction flask was cooled in an ice water bath so that the temperature did not exceed 5°C. To the reaction mixture was added 11.7g (110mmol) of vinylchloro formate over 30 minutes. The reaction mixture was allowed to stir to room temperature overnight. The solvent was removed on a rotary evaporator and the crude product was taken up in ethyl acetate and washed with 2 100mL portions of 2N HCl, then 2 100mL portions of 2N NaOH, then 2 100mL portions of brine. The organics were dried with magnesium sulfate, the solvent removed and the crude product is distilled to obtain the pure product.

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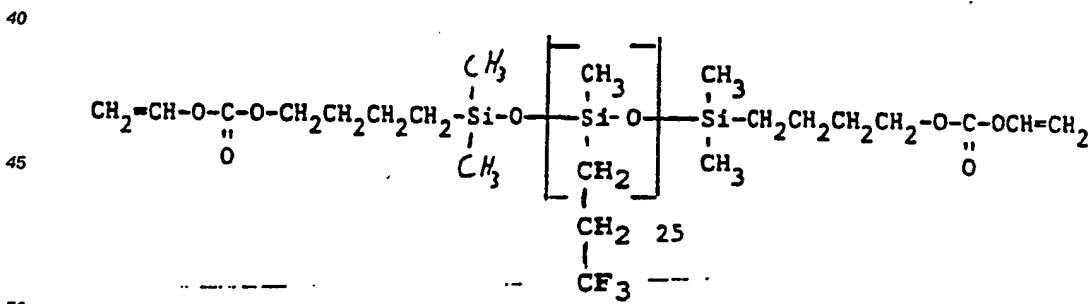
1,3-bis(vinyloxycarbonyloxy)-2,2- bis (vinyloxycarbonyloxymethyl) propane

To a 250ml three neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, and a dropping funnel was added 3.0g (22.0mmol) of pentaerythritol, 7.7g (97mmol) of pyridine and 125mL of anhydrous acetonitrile. The reaction flask was cooled in an ice water bath so that the temperature did not exceed 5°C. To the reaction mixture was added 10.3g (97mmol) of vinylchloroformate over 30 minutes. The reaction mixture was allowed to stir at room temperature overnight. The solvent was removed on a rotary evaporator and the crude product was taken up in ethyl acetate and washed with two 100mL portions of 2N HCl, then two 100mL portions of 2N NaOH, then two 100mL portions of brine. The organic phase was dried with magnesium sulfate, the solvent removed and the crude product distilled to obtain the pure product.



³⁰ V₂DF₂₅

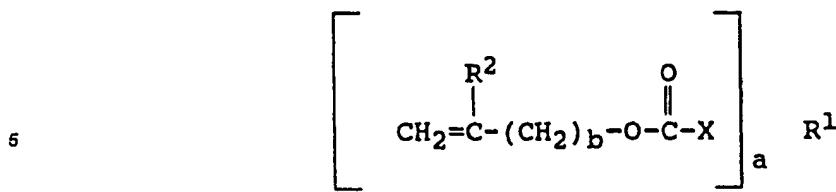
To a 100mL one neck round bottom flask fitted with a magnetic stirrer, and a drying tube was added 5.0g (11.95mmol) of 1,3-bis (4-vinylbutylcarbonate) tetramethyldisiloxane, and 46.6g (99.6mmol) of 1,3,5-methyl,1,3,5-trifluoropropylcyclotrisiloxane. To the reaction mixture was added 0.0679g (0.452mmol) of trifluoromethanesulfonic acid. The mixture was stirred at room temperature for 24 hours then 0.38g (4.52mmol) of sodium bicarbonate was added, and the mixture was allowed to stir an additional 24 hours. The reaction mixture was filtered through 20.0g of activated F20 alumina to give a light yellow oil. The crude product was vacuum stripped at 90°C 0.025 Torr for 4 hours to give the desired product.



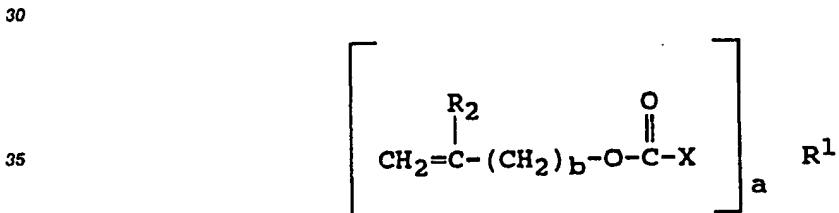
Claims

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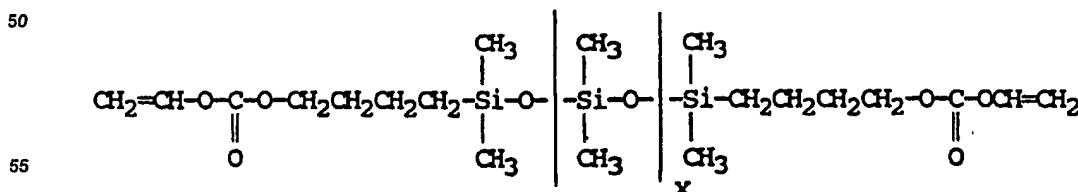
1. A copolymer formed by polymerizing a polymer mixture comprising:
 - (a) a base monomer described by the general chemical formula:



- wherein X denotes an -O-, -S- or -NR³- divalent radical;
- 10 R¹ denotes an organic radical;
- R² denotes -H or -CH₃;
- R³ denotes -H, or a monovalent alkyl radical;
- b equals 0 or 1; and
- (b) a crosslinking agent.
- 15 2. The copolymer of Claim 1 wherein the base monomer is 2-hydroxyethyl vinyl carbonate, 2-hydroxyethyl vinyl carbamate, 3-(2-pyrrolidinone-1-yl)propyl vinyl carbonate, 2-(2-pyrrolidinone-1-yl) ethyl vinyl carbonate, 2,2,2-trifluoroethyl vinyl carbonate, 2,2,2-trifluoroethyl vinyl carbamate, 1,1,1,3,3,3-hexafluoroprop-2-yl vinyl carbonate, 2,2,2-trifluoro-1-phenylethyl vinyl carbonate, trimethylsilylmethyl vinyl carbonate, trimethylsilylvinyl vinyl carbonate, 3-(trimethylsilyl)propyl vinyl carbonate, t-butyldimethylsiloxyethyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate, 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane], 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate, 1,3-bis[4-vinyloxycarbonyloxy]but-1-yl tetramethyl disiloxane, N-[tris(trimethylsiloxy)silylpropyl]-N-methyl vinyl carbamate, N-Vinyloxycarbonyl-N-[tris(trimethylsiloxy)silylpropyl] piperazine, 3-[Tris(trimethylsiloxy)silyl]propylaminoethyl vinyl carbonate, N-(vinyloxycarbonyloxy)-pyrrolidin-2,5-dione, N-(vinyloxycarbonyloxyethyl)-pyrrolidin-2,5-dione, 4-sec-butylphenyl vinyl carbonate, 4-t-butylphenyl vinyl carbamate, 4(t-butyl)cyclohexyl vinyl carbamate, 1-adamantane vinyl carbonate, 1-adamantanemethyl vinyl carbonate, 1-adamantaneethyl vinyl carbonate, or 1-adamantane vinyl carbamate.
- 20 3. The copolymer of Claim 1 or Claim 2, wherein said crosslinking agent is described by the general formula:

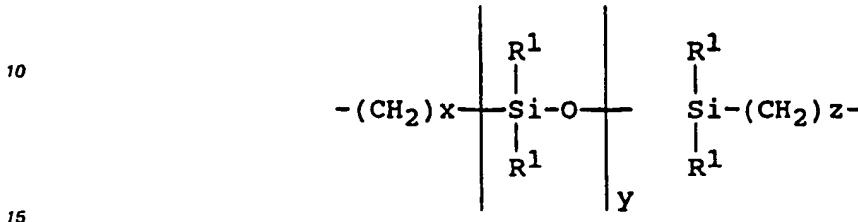


- 35 wherein X denotes an -O-, -S-, or -NR³- divalent radical;
- 40 R¹ denotes an organic radical;
- R² denotes -H or -CH₃;
- R³ denotes -H or a monovalent alkyl radical;
- a equals 2, 3 or 4; and
- b equals 0 or 1.
- 45 4. The copolymer of Claim 3 wherein the crosslinking agent is propargyl vinyl carbamate of 1,3-bis[4-vinyloxycarbonyloxy]but-1-yl]-tetramethyl disiloxane.
5. The copolymer of Claim 3 wherein the crosslinking agent is of the formula:



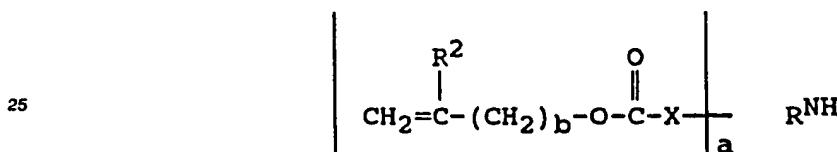
6. The copolymer of Claim 3 wherein the crosslinking agent is 1,2-bis-(vinyloxycarbonyloxy)ethane, $\alpha\omega$ -bis-(vinyloxycarbonyl)triethyleneglycol, $\alpha\omega$ -bis-(vinyloxycarbonyl)polyethylene glycol, $\alpha\omega$ -bis-(Vinyloxycarbonyl) polypropylene glycol, 2,2-dimethyl-1,3-bis-(vinyloxycarbonyloxy)propane, N,O-bis-(vinyloxycarbonyl)-ethanolamine, 2,2-dimethyl-N,N-bis(vinyloxycarbonyl)-1,3-propanediamine, or 1,5-bis-(vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane.

5 7. The copolymer of Claim 3 where a equals 2 and R¹ is of the general formula:



where x and z are 1 to 6, y is on the average between 2 and 200 and R¹ denotes an alkyl radical or fluorinated alkyl radical with 1 to 6 carbon atoms.

8. A hydrogel copolymer formed by polymerizing a prepolymer mixture comprising a non-hydrophilic 20 monomer of the general formula:

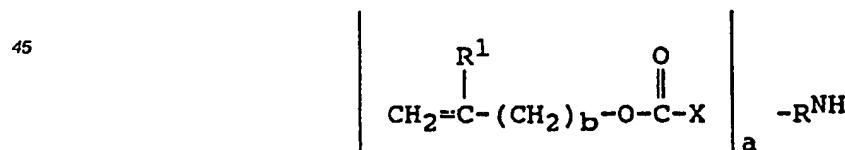


wherein X denotes -O-, -S-, -NR³- divalent radical;
 30 R^{NH} denotes a non-hydrophilic organic radical;
 R³ denotes -H or a monovalent alkyl radical;
 a is 1, 2, 3 or 4;
 b is 0 or 1;
 R² is hydrogen or methyl; and
 35 a hydrophilic monomer; and
 a crosslinking agent.

9. The hydrogel material of Claim 8 wherein the hydrophilic monomer is N-vinyl-2-pyrrolidinone.

10. The novel hydrogel material of Claim 8 or Claim 9 wherein the non-hydrophilic monomer is 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, t-butyl vinyl carbonate, t-butylidimethylsiloxyethyl vinyl carbonate, or 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate.

40 11. A soft, non-hydrogel, copolymer formed by polymerizing a mixture comprising:
 a non-hydrophilic monomer of the general chemical formula:

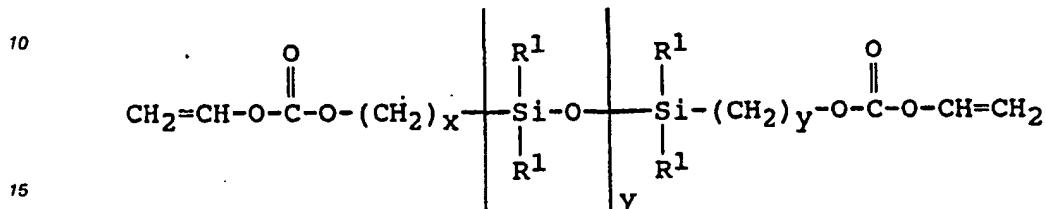


50 wherein R¹ denotes -H or -CH₃;
 R^{NH} is a largely non-hydrophilic organic radical;
 a is 1 or 2; and
 b is 0 or 1;
 55 a hydrophilic monomer chosen from the group consisting of N-vinyl-2-pyrrolidinone and 2-hydroxyethyl-methacrylate, and
 a crosslinking monomer.

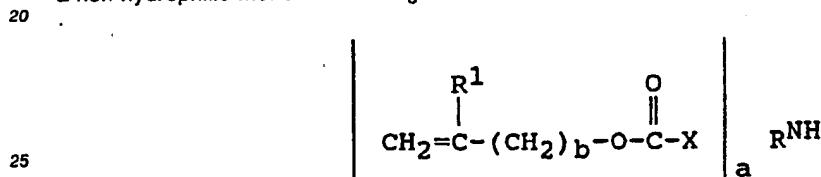
12. The copolymer of Claim 11 wherein the non-hydrophilic monomer is 3[tris(trimethylsiloxy)silyl]

propyl vinyl carbonate, 1,3-bis(4-vinylbutylcarbonate) tetramethyldisiloxane, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate, 3-(Vinyloxycarbonylthio)propyl [tri(trimethylsiloxy)silane], 3-(trimethylsilyl)propyl vinyl carbonat, t-butyldimethylsiloxyethyl vinyl carbamate, trim thylsilylm thyl vinyl carbonate, trimethylsilylethyl vinyl carbonate, trifluoroethyl vinyl carbonate, t-butyl vinyl carbonate, 3[tris(trimethylsiloxy)silyl] propyl vinyl carbonate, 2,2,2-trifluoroethyl vinyl carbamate, 1,1,1,3,3-hexafluoro-2-propyl vinyl carbonate, 2,2,2-trifluoroethyl allyl carbonate, or 2,2,2-trifluoro-1-phenylethyl vinyl carbonate.

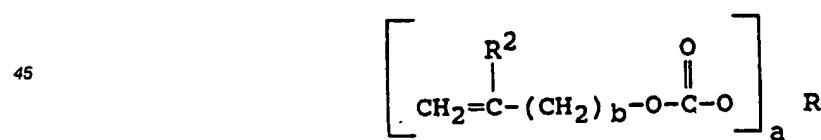
13. The copolymer of Claim 11 wherein the non-hydrophilic monomer is of the general formula:



14. A rigid gas permeable contact lens material comprising:
a non-hydrophilic monomer of the general formula:



- wherein b is 0 or 1;
a is 1, 2, 3 or 4;
30 X denotes -O-, -NH- or -S-; and
 R^{NH} denotes a non-hydrophilic moiety;
 R^1 is H or methyl;
a crosslinking agent; and
1 to 20 wt % of a wetting monomer.
35 15. A compound selected from:
3-(2-pyrrolidinone-1-yl)propyl vinyl carbonate;
2-(2-pyrrolidinone-1-yl)ethyl vinyl carbamate;
2,2,2-trifluoroethyl vinyl carbamate;
1,1,1,3,3-hexafluoroprop-2-yl vinyl carbonate; and
40 2,2,2-trifluoro-1-phenylethyl vinyl carbonate.
16. A compound of the general formula:



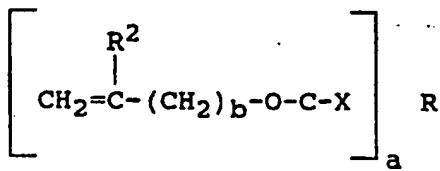
- 50 wherein R^2 denotes -H or $-\text{CH}_3$;
b is 0 or 1;
a is 1, 2, 3 or 4; and
R is an organosilicon radical.
55 17. A compound of Claim 16 selected from trimethylsilylmethyl vinyl carbonate, trimethylsilylethyl vinyl carbonate, 3-(trimethylsilyl)propyl vinyl carbonate, t-butyldimethylsiloxyethyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, 3-(Vinyloxycarbonylthio) propyl-[tri(trimethylsiloxy)silane], 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate, 1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyl disiloxane, N-[tris(trimethylsiloxy)silyl]propyl]-N-methyl vi-

nyl carbamate, N-vinyloxycarbonyl-N' - [tris(trimethylsiloxy)silylpropyl] piperazine, and 3-[tris(trimethylsiloxy)silyl]propylaminoethyl vinyl carbonate.

18. A compound of the general formula:

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wherein a is 1, 2, 3 or 4;

X denotes -O-, -S- or -NR-;

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R² denotes -H or -CH₃;

R³ is -H or -CH₃; and

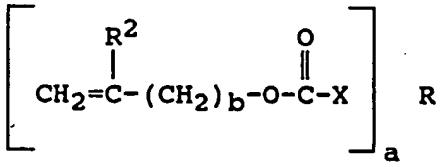
R denotes a cycloalkyl, cycloaryl or heterocyclic radical.

19. A compound of Claim 18 selected from N-(vinyloxycarbonyloxy)pyrrolidin-2,5-dione, N-(vinyloxycarbonyloxyethyl)pyrrolidin-2,5-dione, 4-s-butylphenyl vinyl carbonate, 4-t-butylphenyl vinyl carbonate, 4(t-butyl)cyclohexyl vinyl carbonate, 1-adamantane vinyl carbonate, 1-adamantane methyl vinyl carbonate, 1-adamantane ethyl vinyl carbonate, and 1-adamantane vinyl carbamate.

20. A compound of the general formula:

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wherein a is 1, 2, 3 or 4;

R² denotes -H or -CH₃;

X denotes -S-;

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b is 0 or 1; and

R is an organic radical.

21. Propargyl vinyl carbamate.

22. 1,3-bis[4-vinyloxycarbonyloxy]but-1-yl]tetramethyl disiloxane.

23. 1,2-bis(vinyloxycarbonyloxy)ethane.

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24. α - ω -bis-(vinyloxycarbonyl)triethyleneglycol.

25. α - ω -bis-(vinyloxycarbonyl)polyethylene glycol.

26. α , ω -bis-(vinyloxycarbonyl) polypropylene glycol.

27. 2,2-dimethyl-1,3-bis(vinyloxycarbonyloxy)propane.

28. N,O-bis-(vinyloxycarbonyl)-ethanolamine.

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29. 2,2-dimethyl-N,N-bis(vinyloxycarbonyl)-1,3-propanediamine.

30. 1,5-bis(vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane.

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